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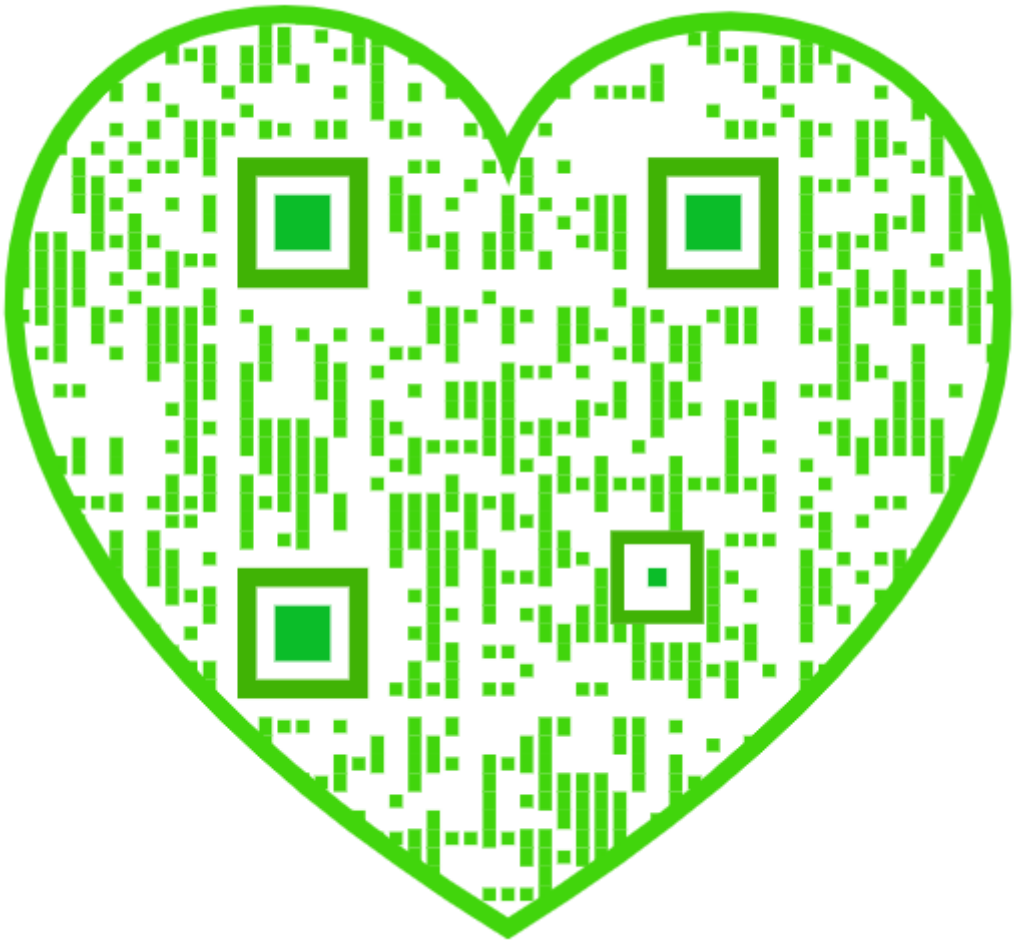

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A Study of the Changes in Skins During Their Conversion into Leather

A thesis submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the University of Michigan

By

Anton Augustus Schlichte

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Meinen lieben Eltern in
Dankbarkeit gewidmet

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INTRODUCTION.

The use of hides both as skins and leather for protection against cold and rain, for weapons, or for ornaments, dates back to the remotest history of man.

While the hides were tanned in the earlier times with the hair on, methods were soon found to remove it and thus improve the product. The first substance used was probably wood ashes and this continued as the standard for some time. After tanneries were established, for up to this time the tanning was done only on a small scale, new substances were sought for, and lime, one of the oldest depilatory agents, was used. The method followed was to slack the lime in pits and soak the hides in a saturated solution of calcium hydroxide. This method although slightly modified has remained practically the same for centuries.

The tanning process was and is in general the following:

1. Hides are soaked to remove blood and dirt and to bring them back as nearly as possible to their original condition.

2. They are placed in pits containing milk of lime, bacteria being always present and sulphides being frequently added, for from 3 to 18 days until the hair "slips" easily, that is, can be easily removed.

3. They are then bated to remove lime and bring the skin into the desired physical condition. The bate may be either acid or bacterial.

4. The next step is the pickling process in which the skins are treated usually with salt and sulphuric acid.

5. Then follows the tanning process proper, which may be either a mineral or a vegetable tannage.

6. The last step is a finishing process.

The entire tanning process has thus far been outlined to show the dependence of the finished product upon the correct performance of each succeeding step of the process. It is only through tests on the finished leather that the effect of any alteration in any step of the process can be detected.

The liming process is the one studied in greatest detail in this paper but any changes due to this operation can be detected only in the finished product. Moreover, the method of soaking must, because of its influence, also be specified. The object of soaking hides is to cause them to resume as nearly as possible their original clean and pliable condition. This part of the process while not so important when green hides are used becomes a matter of great importance when dried hides are to be investigated. The length of soaking, number of changes of water and the acids or alkalies which may have been added, all have an effect on the final product. Should the hides be soaked too long or should the water not be renewed frequently enough, bacteria multiply and a part or, in extreme cases, all of the hide may be lost. On the other hand acids and alkalies cause swelling of the hide and if too much of either be added the hide will be "plumped" too much.[1] This, while not fatal to a good final product, has its disadvantages and as a rule causes trouble.

The object of liming is not alone the removal of the hair but also the loosening of the fiber bundles. More surface is thus exposed and hence the tanning agents are taken up more readily.

[1] Jettmar Handbuch, p. 56.

In the vegetable tannage this makes a heavier leather. In the mineral tannage the loosening of the fiber bundles makes a more pliable leather.[2] The latter object is of great importance in the chrome tannage which is the method most used in manufacturing light or upper leathers. The hides after soaking are placed in pits in which an excess of calcium hydroxide is always present and to which some sodium or arsenic sulphide may or may not have been added. The hides are "hauled," that is, taken out and the lime "bettered" once a day until the hair "slips" easily. It requires much practice and experience before one is able to tell exactly whether a hide is done or not, and the method is not only unsatisfactory but also very unscientific, for the personal equation of the operator plays too important a part. The hides are then soaked in warm water, paddled and beamed. In the latter process the skin is placed over a piece of wood semi-circular in cross section and the hair is removed with a blunt knife. The long hairs comes off very easily but the fine or "ground" hair and the pigment, especially in the case of black skins, cause some trouble. Part of the intercellular substance, corium, "scud" or "gneiss" and some lime soaps[3] are also removed in this treatment

The next operation, "bating," has as its main object complete removal of the lime remaining from the previous treatment. The loosening of the fiber bundles, however, is also materially aided by bating and this, as before mentioned, is, in the case of light leather, of greatest importance. The bates most commonly used owe their activity to bacteria and are frequently more or less unsatisfactory and harmful to the skins. Bates of known bacterial cultures are used somewhat and give good results, but the most common ones consist of organic acids such as butyric, lactic, etc.

The skins are then pickled. The pickling consists usually of a treatment with sulphuric acid and salt. One object is to partially reduce the excessive swelling caused by the bate. Another, without doubt, is to furnish some free sulphuric acid which is considered necessary in the subsequent chrome bath. This sulphuric acid is probably absorbed by the skin and thus carried over to the tan bath. This finishes the treatment received by the

[2] *Gerber*, No. 938, p. 253; Procter's Principles of Leather Manufacturing, p. 126.

[3] Procter's Principles of Leather Manufacture, p. 136.

skins in the "Beam House," which is probably the most important division of the tanning process. The most important part of the beam house work is the liming process, and hence this was made the object of the subsequent investigations. The object was to gain some insight if possible, into this apparently simple but actually very complicated process and to furnish something of practical value to the industry.

It seemed obvious that some accurate way of controlling the liming and of judging the product afterward was absolutely necessary in order that improvements could be noted. The ordinary method of judging the product by the "feel" left much to be desired and it was recognized that the personal equation had to be eliminated as much as possible if anything of real value were to result. The most natural idea was to obtain some means of following the action of the lime step by step. This could not be accomplished with the naked eye and hence the assistance of the microscope was necessary. A review of the literature at hand showed that although considerable work with the microscope had been done the results were not very satisfactory.

Study of Microscopic Changes in Hides During Their Conversion Into Leather.

Some of the earliest work on the cutting of sections of leather was done by Kathreiner in 1879.[4] This work was never published and on inquiring of Prof. Procter it was found that although notes had been preserved, they were in no shape to allow of their being published. Thus we have no authentic record of his work. The next reference found was to some work by Prof. Thomas Palmer.[5] He applied his method to determine the penetration of vegetable tanning agents. The sections were mostly cut by hand. Some sections after dehydration in alcohol and clearing in clove oil were infiltrated with "Strickers" solution (gum arabic and glycerine 3 : 1) and cut with a microtome. In some cases he also dehydrated in alcohol two or three hours, cleared in a mixture of cedar oil and benzol, infiltrated in a mixture one part 50° melting point and two parts 40° melting point paraffine until transparent, and then changed to a bath of two

[4] Procter's Leather Industries Laboratory Book, p. 424.

[5] *Collegium*, 1902, p. 325.

parts 50° melting point and one part 40° melting point paraffine for three or four hours. The mixture of cedar oil and benzol was in the ratio of three to five. He does not tell of any changes noted in the leather, except that the distance to which the tanning agent had penetrated could be noted by differential stains. Moreover he does not give the thickness of the sections cut. Procter, in his Leather Industries Laboratory Book, also speaks of cutting sections by hand and of cutting sections by means of a microtome, but gives no specific directions.

M. Henri Boulanger in an elaborate monograph, "Essais du Cuir dans ses Applications industrielles. Memoires publies par la Societe d'Encouragement pour l'industrie national 1907," part of which is published as "Etude Micrographie du Cuir" in *Bulletin de la Societe d'Encouragement* in 1908, gives some directions for cutting sections. The pieces to be cut are placed 12 hours in a mixture composed of distilled water 5 grams, pharmaceutical glycerine 5 grams, acetone 90 grams. They are then dried and imbedded in hard paraffine and cut. Another method given is to dehydrate in gradually increasing alcohol until absolute is used, to place in xylol, then in melted paraffine 38° to 40°. After several days the tissues are cooled, dried 36 or 48 hours, imbedded in hard paraffine and cut. Although many sections were prepared their thickness is not mentioned. One interesting conclusion of the author is that the elastic fibers are well preserved and that to them the leather owes its strength and pliability, while the connective tissue has been totally changed. This is a remarkable conclusion when one takes into consideration that less than 3 per cent. of the skin is elastic tissue and more than 95 per cent. is connective tissue.[6] Moreover the elastic fibers have little elasticity and are the first to rupture when the skin is stretched. Their chief function appears to be that of support.[7]

Andreis, in an article on "The Process of Liming"[8] speaks of "taking a transverse section of the hide and noting no horizontal layers or channels." He does not give any methods for cutting the sections and presumably means that they are to be cut by hand.

[6] Reimer, *Ding. Poly. Jour.*, No. 205, p. 149 (1872).

[7] Hyde, Diseases of the Skin, p. 22 (1909).

[8] JOURNAL, Am. Leather Chem. Assoc., Vol. VII, p. 609 (1912).

As none of the references quoted gave definite, concise and adequate directions for preparing sections, experiments were resorted to, in order to find a way to prepare good sections by some simple and quick method Having no landmarks to guide us, much time was spent in going astray. At this time certain sections of rocks were being made by grinding and this method appeared feasible for leather. The piece of leather to be ground was placed in Canada balsam in a tube in hot water and suction applied. After two to four hours the leather seemed impregnated with balsam and was removed, mounted on a piece of plate glass 1 inch square and ground with a carborundum wheel until a flat surface was obtained. The piece was then turned over and mounted and the grinding continued, until the section was fairly thin. Then a finer wheel was used, until the section became very thin. It was removed, turned over and mounted on a glass slide and the grinding resumed, until the section was as thin as could be obtained. These sections showed some fiber bundles but were unsatisfactory in three ways. The process was too slow, the sections too thick, and a complete section could not be obtained as some parts were always torn away in grinding.

Methods of Imbedding and Cutting Tissues.

Leather is harder and tougher than ordinary tissue. It is dense and requires an unusually long period of infiltration. It is tough and offers great resistance to the knife so that the infiltration must be very thorough before good sections can be obtained.

Methods of cutting sections after imbedding in paraffine and celloidin and after freezing were studied. Various modifications were tried and those giving best results are described in detail, although they are merely modifications of methods used in pathology.

The method of imbedding in paraffine involves the following steps.

1—95 per cent. alcohol 24 hours, change after 12 hours.
2—Absolute alcohol 24 hours, change after 12 hours.
3—Xylol, 1 hour.
4—Xylol, 2 hours.
5—Paraffine 42° melted in an oven from 12 to 24 hours depending on size of piece used.
6—Paraffine 52° from 24 to 48 hours depending on size of the piece.

The piece is then taken from the molten paraffine and imbedded according to the following procedure. A small dish is greased with tincture of green soap or glycerine and placed in cold water. Clean 52° paraffine is melted with a free flame and the molten paraffine is allowed to drop into the dish until it has attained a depth greater than the thickness of the piece to be imbedded. As soon as a film of hardened paraffine has formed on the bottom the tissue is removed from its previous bath and placed face down in the dish. The surface of the melted paraffine is now cooled by blowing on it, and as soon as a fairly thick film has formed the whole dish is plunged into ice water.

In spite of all precautions taken this method was not satisfactory. All attempts to cut sections of a satisfactory thickness were unsuccessful as the tissue was either pulled away from the imbedding material or was torn by the knife. In fact, no complete thin section could be obtained by this method. Other methods based on paraffine infiltration using acetone, clove oil, oil of bergamot and aniline were tried and the results were unsatisfactory. Even infiltration with paraffine in solution, that is, in benzol or xylol, gave poor results. This seems to show that ordinary methods cannot be used and that methods like the one used by Boulanger[9] "infiltrating in melted paraffine 15 minutes and then blocking in hard paraffine" cannot give good results.

The next method tried was the celloidin method. In this the dehydration was carried over a longer period so that the presence of any moisture was precluded. The procedure was as follows:

1—80 per cent. alcohol 12 hours.
2—95 per cent. alcohol 48 hours, changed every 24 hours.
3—Absolute alcohol 48 hours, changed every 24 hours.
4—Absolute alcohol and ether (equal parts) 24 hours.
5—1 per cent. celloidin 96 hours.
6—2 per cent. celloidin 120 hours.
7—5 per cent. celloidin 168 hours.
8—10 per cent. celloidin 6 days to 2 weeks depending on the size of sample used.

In order that a number of pieces might be imbedded simultaneously they were held in clips tied to strings, which led through holes, in the wooden cover of a shallow dish. This dish was filled

[9] Bulletin de la Societe d'encouragement, p. 250 (1907).

with a 10 per cent. solution of celloidin, the cover put on and the ether and alcohol allowed to evaporate. The tissues were then cut out, trimmed and mounted on wooden blocks. They were cut in a microtome under a constant flow of 80 per cent. alcohol. The sections obtained by this method, after long practice, were as thin as 5 or 7 microns and averaged about 10 to 18 microns. These could be examined even with an oil immersion lens. This method while giving excellent results had as a very serious disadvantage the long time necessary for good results. Many attempts were made to shorten this method but none gave good results. A very long time is absolutely necessary for perfect infiltration.

Believing that the added knowledge gained by experience might after all, enable us to use the paraffine methods, these were again tried. The results while better than those first obtained, still left much to be desired. The leather tore away from the paraffine very easily and it was impossible to cut good sections. The paraffine methods had so many advantages both as to quickness and simplicity, that many modifications of the method previously given, were repeatedly tried. The conclusion finally reached was, that none of the paraffine methods would give good results. Methods using beeswax, gum arabic, etc., were tried and also failed to give good results.

The only short method which appeared promising was the freezing method and this was then tried. This method had the obvious advantage of great saving in the time required to obtain complete sections. The method was very simple and, although much practice and experience were necessary before good sections were obtained, the results justified the time spent in acquiring the technique. The sample to be sectioned was cut from calfskins, 1 by 2 centimeters and if wet, mounted directly. If dry, it was first soaked in water until thoroughly moistened and then mounted upon the base plate of a Bardeen microtome and covered with a thick solution of gum arabic. The liquid carbon dioxide was then turned on and the pieces were frozen very gradually. When the right degree of hardness has once been obtained the piece should never be allowed to warm up and should never be frozen again. This is of great importance as several

freezings will cause important changes in the structure.[10] The greatest changes are caused by over freezing and if this is done excessively, the piece used may crumble and become worthless. A slight fixation of the tissue in 10 per cent. formol[11] prevents most of the changes due to freezing. The sections when cut are placed in a dish filled with water. They are then transferred by means of a brush or section lifter to a 10 per cent. dextrin solution which is kept warm, and floated onto a glass plate, dried a few minutes, soaked in absolute alcohol until clear and coated by pouring over them a 1 or 2 per cent. solution of celloidin. The plates are placed in warm water and left until the thin celloidin sheet floats off. They can now be handled easily and quite roughly without any danger of damage. They can be stained with alcoholic or aqueous solutions of various dyes. A water solution of eosin and also a double stain, first in Weigert's haematoxylin and then in Van Giesens[12] mixture were used. The latter gave excellent results and enabled one to distinguish the various kinds of fibers present, with great certainty.

The sections were not so thin as those obtained by the celloidin method, averaging only 35 to 40 microns, but this was thin enough to allow the use of any high power objectives except the oil immersion. The sections were very delicate and required great care in the preliminary handling. The method requires little time. A skilled operator can fix, freeze, stain and mount a complete section in 30 or 40 minutes. In some cases the time required is greater depending on the ease with which the piece in question can be cut. Sections from heavy hides during the liming require much longer, as the tissue is very delicate and flabby and tears very easily. After the hide has been in a tan liquor it can be cut very rapidly. This method has not only the advantage of speed but also is better in that the tissue is practically the same as it was before cutting. The method does not subject the tissue to such severe treatment as for instance the dehydration with absolute alcohol, which is necessary in the case of the celloidin and paraffine methods. It is true that freezing may dehydrate in a certain sense, but the following immersion in water probably

[10] Warthin Practical Pathology, p. 215.
[11] Warthin Practical Pathology, p. 216.
[12] Warthin Practical Pathology, p. 260.

allows the tissue to resume its previous condition. This seems logical, since the freezing lasts a very short time, from 5 to 10 minutes at the most.

Study of Changes in Structure During Tanning.

Before proceeding to the experimental study of tissues prepared in the laboratory a considerable number of commercial products were examined. Sections were made of various commercial leathers such as dongola, waterproof, wax upper, plow grain, flesh splits, badger sides, oil grain, reliance calf, dull romar sides, kangaroo calf and others. These gave some idea of how a finished leather looked. Through the courtesy of Mr. Carl E. Schmidt of Detroit, pieces were cut daily from a particular calfskin as it went through his tanning process and sent for examination. As soon as these samples were received a section was made by the freezing method and a piece started by the slow celloidin method. This set was kept as a standard of a good product and will be referred to as S-22. This set did not, however, entirely fulfill its purpose, because the necessity of knowing the exact location and orientation of the pieces cut from the hide was not discovered until later. This was shown by an examination of pieces cut in a systematic manner from a finished calfskin (Experiment S-18). Samples were taken from this leather at the butt, right and left flank, and neck and carefully infiltrated with celloidin. Sections were cut both parallel and at right angles to the grain. The sections showed a great difference in structure between pieces cut from the flank and from the butt. These show the flank to have a much smaller amount of connective fibers than the butt and neck. Moreover, the fiber bundles of the flank are further apart and in general form a looser network. The connective tissue is more wrinkled that is, the folds in the individual fiber bundles are more numerous. This apparently accounts, at least partially, for the looseness of the flank after tanning.

This difference between various portions of the same skin was further studied in series S-26, by tanning two pieces of calfskin cut so that one piece was almost entirely flank while the other was along the backbone. Small pieces were cut daily from adjacent portions of each skin, one from the backbone and the other

from the edge of the flank, and sections were prepared by the freezing method using the Van Giesen stain. Sections were cut both parallel and at right angles to the backbone in each instance. These showed the same looseness in structure in the fresh flank as was evident in the finished leather.

This subject was pursued still more systematically in Series S-36 where a whole calfskin was trimmed to an approximate rectangle and divided into six pieces. This work is referred to again in the discussion of volume changes where the details are given.

Through the courtesy of V. A. Wallin of Grand Rapids, samples of a certain cow hide were sent throughout the tanning process. The pieces were taken so that the sections made therefrom could be cut parallel and at right angles to the backbone. Samples were received during the following stages of the tanning process. All sections were cut by the freezing method.

No. 1.—Washed hide—originally a green salted one.
No. 2.—After 24 hours in lime.
No. 3.—After 72 hours in lime.
No. 4.—After 96 hours in lime.
No. 5.—Out of hot water.
No. 6.—Into cold water.
No. 7.—Out of cold water.
No. 8.—Out of rockers—in 8 days.
No. 9.—Out of hang yard—in 4 days.
No. 10.—Out of first layer—in 5 days.
No. 11.—Out of second layer—in 9 days.
No. 12.—Out of third layer—in 15 days.
No. 13.—Out of fourth layer—in 22 days.
No. 14.—Out of fifth layer—in 28 days.
No. 15.—Out of wet dip—in 15 days.
No. 16.—Out of tempering vats—in 2 days.
No. 17.—Out of bleach.
No. 18.—Out of oil wheel.
No. 19.—Finished leather.

In these various experiments about 125 different blocks were prepared, from which 600 specimens were cut, stained and mounted. A careful examination of all these sections gave, however, rather meager results. The changes from day to day are so gradual and the differences in structure of different portions of the same hide are so pronounced that it is extremely difficult

to state the cause for any differences observed. The fiber bundles become partially separated into fibrils in the liming process, but it could not be determined whether these fibrils are hollow or solid. In the bark-tanned process the interstices become filled with solid material so that the leather becomes firm and of more uniform structure. In chrome-tanned leather, the interstitial spaces are even greater than in the soaked hide and the fiber bundles and fibrils are sharply defined. The flank is undoubtedly composed of larger fiber bundles than the butt or shoulder and in the former there are larger spaces between these bundles than in the latter.

The idea first held that the microscopic method could be used in the tannery, as an accurate check on the process, had to be abandoned. The great difficulty was that in a given skin, pieces from different parts showed such differences in structure that even after long experience one could not tell whether the differences shown were inherent in the skin or due to the influence of the treatment.

Changes in Volume of Hides During Liming Process.

Changes in the volume of hides in the limes are so great as to be readily noticed. There have, however, been no quantitative data published on this point. The apparatus used for these measurements is shown in Fig. 1.

It consists of a brass cylinder *A*, 2.5 inches in diameter and 15 inches high. At the bottom a small brass tube *B*, 0.25 inch in diameter leads to an upright 100 cc. glass stoppered burette, *C*. The cover *D* screws on to the cylinder by means of a very fine thread, which insures a water-tight joint. The cover is divided into 30 equal divisions on the edge *K* and a vertical mark is made on the cylinder, permitting the cover to be screwed down to a definite point or reading. In the center of the cover a hole is bored into which a pipe with outside threads *E* is soldered. Another pipe with inside threads *F* fits over *E*. A glass tube *G* with a fine string around it is inserted into *E* through *F* and screws tight by means of *F*. This joint is also water tight, if the thread has been previously greased. The threads of cover *D* are also greased, anhydrous lanoline proving a good material for this purpose. The glass tube *G* has a mark, to which the liquid

used is allowed to ascend before a reading is taken. This is done by keeping burette *C* filled to a mark, higher than the top of the cylinder. The cylinder is lacquered on the inside and can be used for lime.

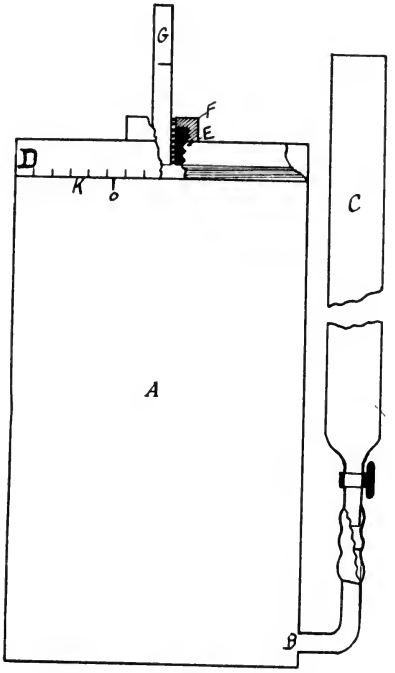


FIG. 1.

To obtain some idea of the accuracy of the measurements made, the following experiments on the volume of a glass stopper are given:

Number of test	I	II	III	IV	V
Zero reading in cc.	25.45	58.9	20.70	59.85	57.65
Taken out in cc.	50.00	0.0	50.0	0.0	0.0
Total cc.	75.45	58.9	70.70	59.85	57.65
Final reading	34.50	17.9	29.95	18.90	16.65
Volume in cc.	40.95	41.00	40.75	40.95	41.00

The average volume was 40.93 cc. and the maximum error was 0.18 cc. in 40.93 cc. equaled 0.44 per cent. This error, however, was relatively small because the stopper could be dried and

always brought to a certain condition of surface moisture, not a varying one, as was the case with skins. The removal of liquid which was made necessary whenever the volume exceeded about 50 cc. was best accomplished by means of a pipette. The liquid was drawn up into the burette after a measurement had been taken, by means of a rubber tube attached to the burette and to a suction pump. The procedure was as follows: Some of the liquid to be used was put into the cylinder *A* and the burette filled by applying suction. The stop cock was closed, the cylinder filled and the cover screwed down to a certain mark. The stop cock was then opened and the liquid allowed to run into the cylinder until the meniscus in the glass tube *G* was even with the mark. A reading of the burette gave the zero reading. The liquid was sucked back into the burette, the cover taken off, the sample placed in the cylinder and, if the volume was large, some of the liquid was pipetted off. The cylinder was then closed and a reading taken as before. This gave a final reading and from it and the zero reading the volume was easily calculated. The skin to be measured was always dried with a moist cotton cloth which was wrung as dry as possible. The skin was always measured in the same liquid in which it was at that stage of the experiment, that is, when in the limes, in lime water; when in pickle, in pickle solution, etc. Duplicate determinations on pieces of skin whose volume was from 200 to 400 cc. agreed within about 1 cc. When dry skins were to be measured the cylinder was filled with water. The skin naturally absorbed some water, but if the experiment was performed rapidly, the error was not large, as was shown by the following experiment:

Zero reading	56.75	
Final reading	14.25	
Volume	42.50	after 1 minute
	42.65	after 2 minutes
	42.85	after 3 minutes
	42.70	after 4 minutes
	42.95	after 5 minutes
	43.00	after 10 minutes
	43.1	after 15 minutes
	43.3	after 20 minutes

The change in volume due to water absorption is very small.

To test the absolute accuracy of the method this same piece of skin was dried and its volume remeasured. The agreement was within 0.5 cc. One difficulty to be guarded against in measuring dry skins is the tendency of air bubbles to adhere to the hairs. This can be avoided by shaking the whole apparatus just prior to taking measurements.

EXPERIMENTAL WORK ON VOLUME CHANGES OF CALFSKINS.

Nine sets of tests involving measurements of volume changes on twenty-one different pieces of skin are reported here. Microscopic sections from some of these sets have been referred to previously. The full data are given under the separate headings, but the sets may be outlined as follows:

S-25—A half-calfskin split along the backbone and trimmed, cut into three pieces of about equal size at right angles to the backbone. Carried through the tanning process. Changes in weight of the pieces were also noted and the density at each stage computed.

S-26—A half calfskin as above was carried through the whole process as one unit. Measurements of surface area and weight were included.

S-27—A piece of calfskin carried through the limes only.

S-28—Duplicate of 26.

S-29—A half calfskin was cut parallel to the backbone to make one piece back and the other flank. Carried through the limes.

S-31—Duplicate of 29, but carried only through soaking process.

S-36—A whole calfskin trimmed and cut into six pieces. Protective action of lime soap tested.

S-39—Duplicate of 25.

S-39B—Duplicate of 29.

EXPERIMENT S-25.

A dry salted calfskin was split along the backbone and one half was trimmed and cut into three pieces of about equal size at right angles to the backbone. The piece nearest the head was marked I, the middle piece II, and that nearest the tail III. These pieces were soaked in water three days, the water being changed every 12 hours. They were then placed in limes, made by using 5

grams of slaked lime to 400 cc. of water, a portion of old lime being added to inoculate the new lot. It was bated in a bran drench and pickled in salt and sulphuric acid solution made by taking 3 grams of concentrated sulphuric acid and 36 grams of salt in 850 cc. of water. The tannage was by Dennis's one-bath chrome method. In the following tables and curves the changes in volume and weight are calculated on the volume and weight of the skin after 72 hours soaking in water instead of on the dry skin. This follows the usual custom of basing all computations on the wet hide and allows comparison to be made with green hides.

EXPERIMENT S-25.—CHANGES IN DENSITY.

Condition of skin.	Number I	Number II	Number III
In water 72 hours.....	1.08	1.10	1.12
In lime 24 hours.....	1.09	1.10	1.13
In lime 48 hours.....	1.08	1.06	1.06
In lime 72 hours.....	1.08	1.09	1.05
In lime 96 hours.....	1.05	1.05	1.03
In lime 120 hours.....	1.06	1.07	1.04
In lime 144 hours.....	1.07	1.08	1.10
In lime 168 hours	1.07	1.08	1.09
In lime 192 hours.....	1.07	1.07	1.08
Unhaired and fleshed ...	1.07	1.05	
Bated	1.04	1.03	
Pickled	1.06	1.06	
Tanned	1.06	1.07	

EXPERIMENT S-26.

A dry salted calfskin was trimmed and split along the backbone. It was intended to carry a half-skin through the experiment as one piece but the apparatus for volume measurements was found to be too small so it was split into two pieces. The figures for the two pieces have been added together so that the result is reported as if it had been kept as one piece. Measurements are reported on volume, weight, area and density throughout the tanning process. These pieces were soaked for 24 hours in water, the latter being changed after 12 hours. The lime used was made by dissolving 5 grams of dry hydrated lime in 400 cc. of water. The pieces were placed in this solution for ten days. The lime was changed every 48 hours and a new lime of the same concentration was prepared. After liming until the hair slipped easily, the skins were placed in warm water for a few minutes, unhaired and fleshed.

EXPERIMENT S-25.—CHANGES IN WEIGHT.

Condition of the skin	Number I			Number II			Number III		
	Weight in grams	Increase in grams	Per cent. increase	Weight in grams	Increase in grams	Per cent. increase	Weight in grams	Increase in grams	Per cent increase
In water 72 hours.....	90.0	0.0	0.0	85	0.0	0.0	86.7	0.0	0.0
In lime 24 hours.....	120.0	30.0	33.3	99	14.0	16.5	110.0	23.3	26.7
In lime 48 hours.....	124.0	34.0	37.8	103	18.0	21.2	116.0	29.3	33.8
In lime 72 hours.....	129.0	39.0	43.3	110	25.0	29.4	123.0	36.3	41.9
In lime 96 hours.....	132.0	42.0	46.7	114	29.0	34.1	129.0	42.3	48.8
In lime 120 hours.....	130.0	40.0	44.5	112	27.0	31.7	125.0	38.3	44.2
In lime 144 hours.....	136.0	46.0	51.1	111	26.0	30.6	134.0	47.3	54.6
In lime 168 hours.....	138.0	48.0	53.3	111	26.0	30.6	138.0	51.3	60.6
In lime 192 hours.....	138.5	48.5	53.9	112	27.0	31.8	134.0	47.3	54.6
Unhaired and fleshed..	105.0	15.0	16.7	92	7.0	8.2	—	—	—
Bated.....	135.0	45.0	50.0	102	17.0	20.0	—	—	—
Pickled.....	123.0	33.0	36.7	102	17.0	20.0	—	—	—
Chrome tanned	124.0	34.0	37.8	104	19.0	22.4	—	—	—

EXPERIMENT S-25.—CHANGES IN VOLUME.

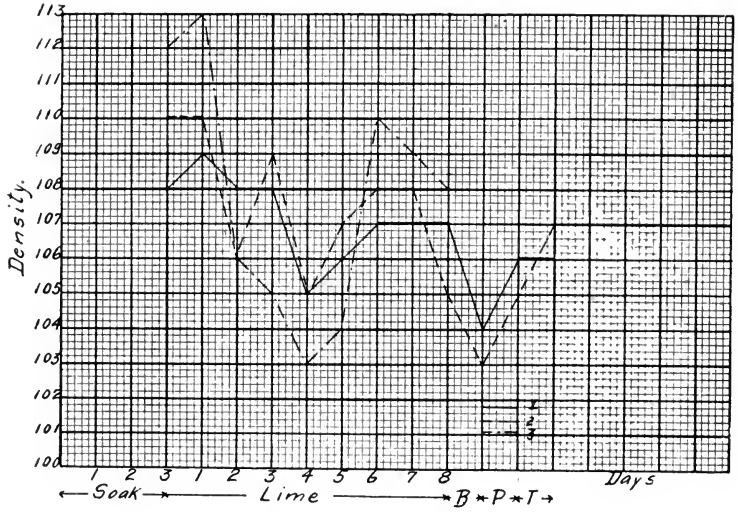
Condition of the skin	Number I			Number II			Number III		
	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase
Dry salted	32.2	—51.0	—61.3	27.7	—50.0	—64.4	26.4	—50.7	—65.8
In water 18 hours	66.7	—16.5	—19.8	56.7	—21.0	—27.0	—	—	—
In water 72 hours	83.2	0.0	0.0	77.7	0.0	0.0	77.1	0.0	0.0
In lime 24 hours	110.6	27.4	32.7	90.0	12.3	15.8	97.4	20.3	26.3
In lime 48 hours	114.4	31.2	37.5	97.4	19.7	25.4	109.9	32.8	42.5
In lime 72 hours	119.8	36.6	40.0	101.0	23.3	30.0	116.9	39.8	51.6
In lime 96 hours	125.9	42.7	51.3	108.3	30.6	39.4	125.0	47.9	62.1
In lime 120 hours	122.7	39.5	47.5	105.2	27.5	35.4	120.7	43.6	56.6
In lime 144 hours	127.2	44.0	52.9	102.4	24.7	31.8	121.9	44.8	58.1
In lime 168 hours	129.0	45.8	55.0	102.3	24.6	31.7	126.8	48.7	63.2
In lime 192 hours	129.2	46.0	55.3	104.3	26.6	32.2	124.7	47.6	61.7
Unhaired and fleshed..	98.2	15.0	18.0	87.5	9.8	12.6	—	—	—
Bated.....	130.4	47.2	56.7	98.8	21.1	27.2	—	—	—
Pickled.....	116.2	33.0	41.0	96.2	18.5	23.8	—	—	—
Chrome tanned	117.5	34.3	41.2	97.5	19.8	25.5	—	—	—

EXPERIMENT S-26.—CHANGES IN VOLUME, WEIGHT, AREA AND DENSITY.

Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in grams	Increase in grams	Per cent. increase	Density	Area in sq. in.
Dry salted	148.7	—219.6	—56.9	170	—235	—58.0	1.14	198
In water 24 hours	368.3	0.0	0.0	405	0.0	0.0	1.10	252
In lime 24 hours	500.6	123.3	34.3	543	138	34.1	1.09	254
In lime 48 hours	535.4	167.1	43.3	572	167	41.3	1.07	254
In lime 72 hours	566.8	198.5	51.4	600	195	48.2	1.06	256
In lime 96 hours	570.2	201.9	52.3	605	200	49.4	1.06	249
In lime 120 hours	581.3	213.0	55.2	613	208	51.4	1.05	249
In lime 144 hours	582.0	213.7	55.3	626	221	54.6	1.08	250
In lime 168 hours	610.2	241.9	62.6	643	238	58.8	1.05	250
In lime 192 hours	606.3	238.0	61.6	650	245	60.5	1.07	248
In lime 216 hours	614.7	246.4	63.8	657	252	62.3	1.07	246
In lime 240 hours	605.5	237.2	61.4	650	245	60.5	1.07	245
Unhaired and fleshed	407.9	39.6	10.3	436	31.0	7.7	1.07	242
Bated	384.6	16.3	4.2	404	—1.0	—0.5	1.06	247
Pickled	335.2	—33.1	—8.6	374	—31	—7.7	1.12	249
Chrome tanned	347.3	—21.0	—5.4	382	—23	—5.8	1.10	209*

* This figure for area is of the dry leather.

EXPERIMENT 25.—DENSITY.

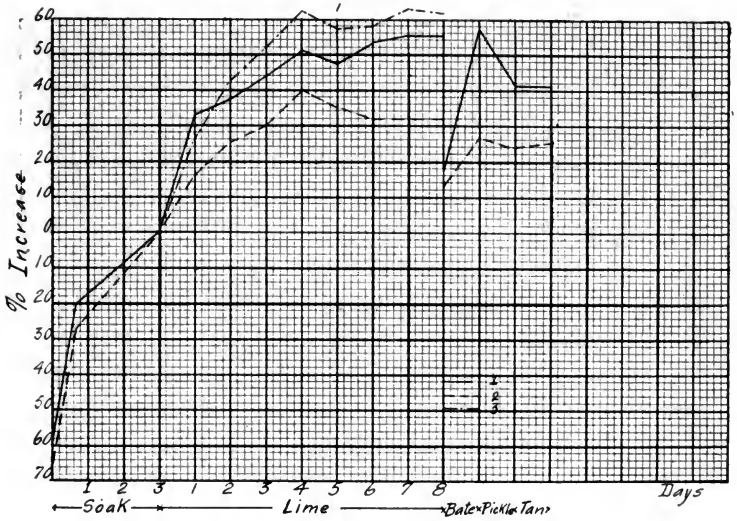


EXPERIMENT 25.—WEIGHT.

Per cent. increase on third soaked weight.

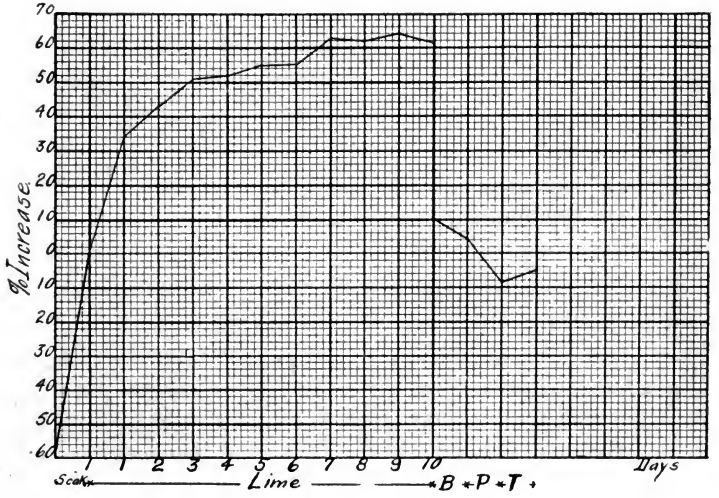
EXPERIMENT 25.—VOLUME.

Per cent. increase on third soaked volume.



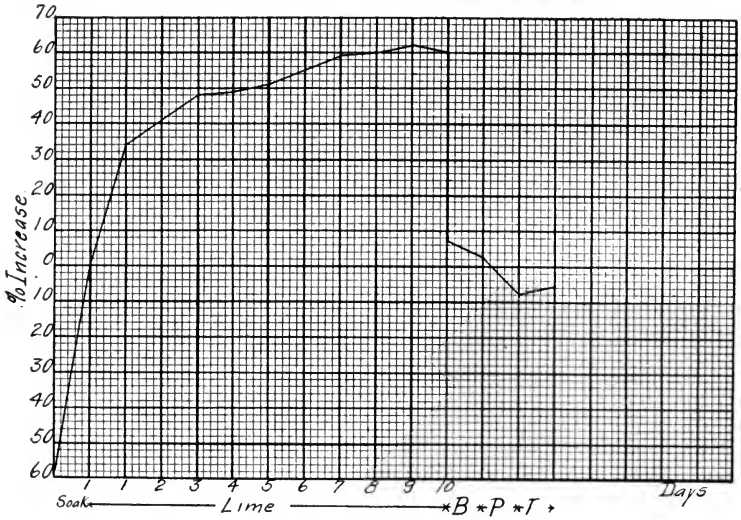
EXPERIMENT 26.—VOLUME.

Per cent. increase on 24-hour soaked volume.

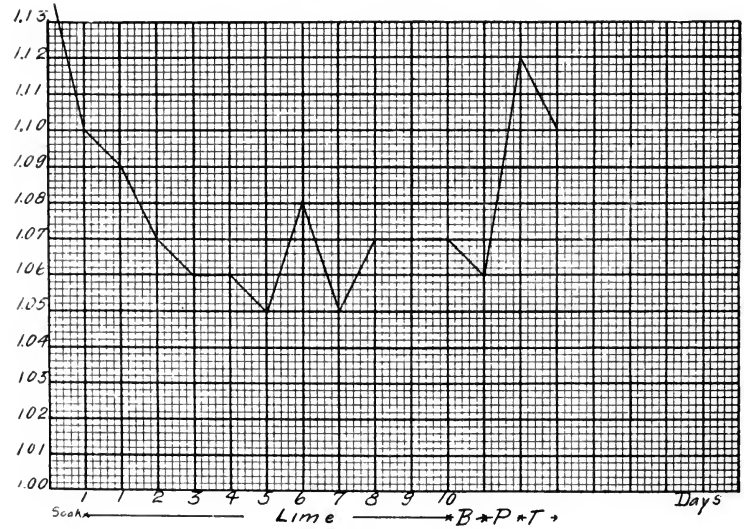


EXPERIMENT 26.—WEIGHT.

Per cent. increase on 24-hour soaked weight.



EXPERIMENT 26.—DENSITY.



The samples were bated three hours in an N/10 solution of lactic acid, in a drum. They were pickled about five hours in an N/50 solution of salt and sulphuric acid. They were then placed in a drum with a normal salt solution for one hour and chrome-tanned by the one-bath process. Sections were also cut daily during this series, as has been mentioned in the discussion of the microscopic study. The results are given in the accompanying table and curves.

Experiment S-27.

In this test a piece of dry salted calfskin was used. It was soaked in water 24 hours. The water was changed after 12 hours. A lime solution containing 5 grams of slaked lime in 400 cc. of water was used to unhair the skin. The hide was in the limes seven days. Sections and volume measurements were made daily and the results tabulated.

EXPERIMENT S-27 CHANGES IN VOLUME, WEIGHT AND DENSITY.

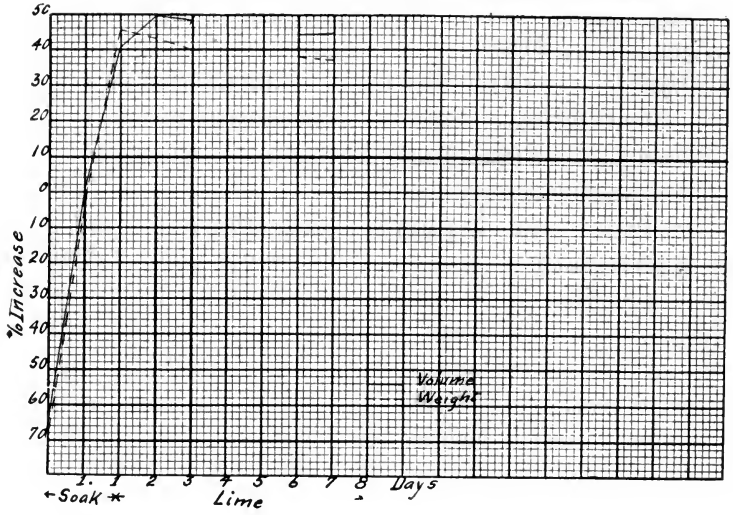
Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in g.	Increase in g.	Per cent. increase	Density
Dry salted.....	83.3	—154.6	—65.0	92	—169	—64.7	1.10
In water 24 hours.	237.9	0.0	0.0	261	0.0	0.0	1.10
In lime 24 hours..	335.6	97.7	41.1	380	119	45.6	1.12
In lime 48 hours..	356.2	118.2	49.8	374	113	43.3	1.05
In lime 72 hours..	354.1	116.2	48.9	365	104	39.9	1.03
In lime 144 hours.	342.4	104.5	44.0	360	99	37.9	1.05
In lime 168 hours.	343.6	105.7	44.5	357	96	36.8	1.04

Experiment S-28.

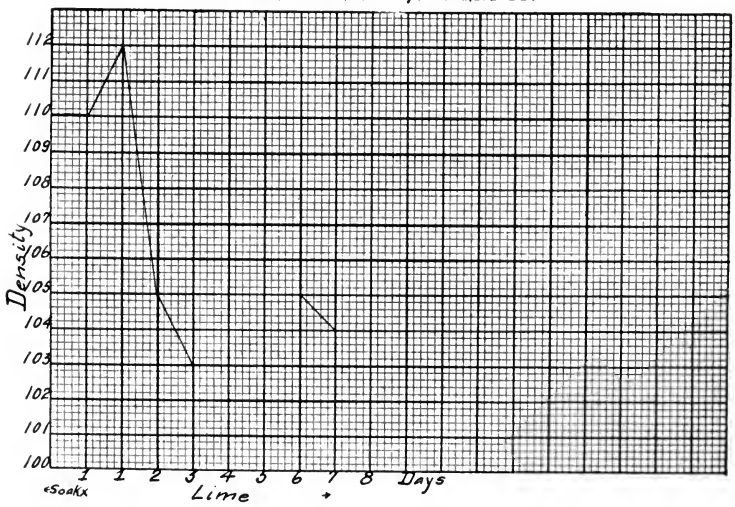
In this experiment a piece of dry salted calfskin was used. The piece of skin was soaked in water 24 hours, the latter having been changed after 12 hours. The limes used were of the same concentration as in Experiment 26. The pieces of hide were limed 6 days. Volume, weight and area measurements were made daily. The skins were limed, unhaired and fleshed, bated in an N/10 solution of lactic acid and followed by a bran infusion. They were pickled in an N/50 solution of sulphuric acid and salt and tanned by the method given in the previous experiment. The product was fair. Analysis showed 5.6 per cent. ash while a standard sample had 5.0 per cent. ash. The measurements taken are in the following table. The increase and percentage increase in weight and volume are all computed on the volume and weight after 24 hours soaking in water.

EXPERIMENT 27.

Per cent. increase on 24-hour soaked volume and weight.



EXPERIMENT 27.—DENSITY.



EXPERIMENT S.28 CHANGES IN VOLUME, WEIGHT, AREA AND DENSITY.

Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in g.	Increase in g.	Per cent. increase	Area in sq. in.	Density
Dry salted	122.6	—181.7	—59.7	135	—191	—58.6	135	1.10
In water 24 hours .	304.3	0.0	0.0	326	0.0	0.0	161	1.07
In lime 24 hours ..	427.2	122.9	40.3	474	148	45.4	161	1.11
In lime 48 hours ..	453.2	148.9	48.8	482	156	47.9	165	1.06
In lime 72 hours ..	454.2	149.9	49.3	483	157	48.1	163	1.06
In lime 96 hours ..	455.1	150.8	49.5	484	158	48.5	164	1.06
In lime 120 hours .	476.0	171.7	56.5	501	175	53.7	164	1.05
In lime 144 hours .	463.0	158.7	52.1	497	171	52.5	160	1.07
Unhaired and fleshed	220.2	— 84.1	—27.6	231	— 95	—29.1	178	1.05
Bated	184.5	—119.8	—39.3	192	—134	—41.1	—	1.04
Pickled	129.3	—175.0	—57.5	145	—181	—55.5	166	1.12
Chrome tanned....	142.5	—161.8	—53.1	158	—168	—51.5	151	1.11

EXPERIMENT S-29.

In order to show whether the flank absorbs more water than the butt, a piece of each kind was used in this experiment. Number one was a piece of calfskin butt and number two, a piece of flank from the same skin. These pieces were always treated in the same manner, in the same solutions. The hides were soaked 48 hours in water, this being renewed every 12 hours. The limes contained 5 grams slaked lime per 400 cc. of water. The liming continued for 4 days and during this time volume measurements were made daily. The results follow:

EXPERIMENT S-29.—CHANGES IN VOLUME OF BUTT AND FLANK.

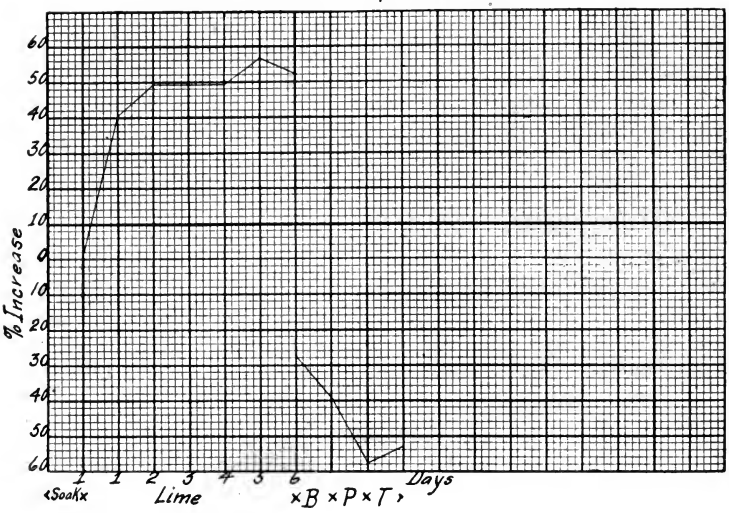
	Number I, butt		Number II, flank	
Condition of the skin	Volume in cc.	Per cent. increase	Volume in cc.	Per cent. increase
In water 48 hours	87.1	—	134.8	—
In lime 24 hours	126.2	44.8	208.4	54.7
In lime 72 hours	138.2	58.8	244.8	82.2
In lime 96 hours	141.7	62.7	258.4	92.0

EXPERIMENT S-33.

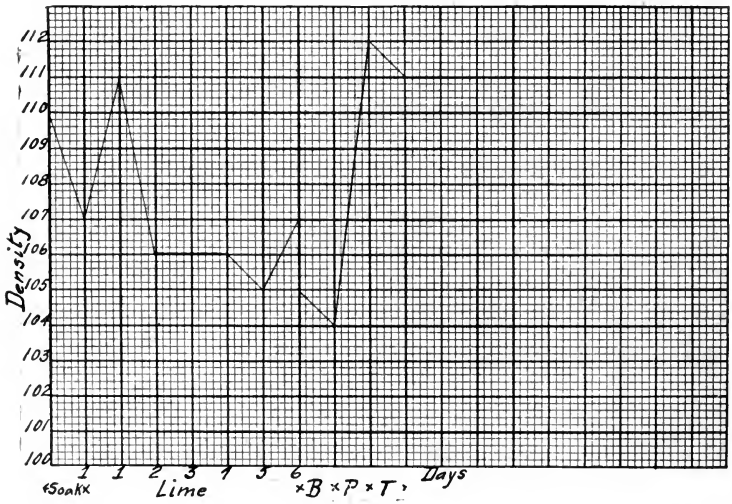
The following experiment was made with pieces of dry salted calfskin. Two pieces were taken; number one being from the flank and number two from the butt. The hides were soaked 24 hours in water, this being changed after 12 hours. The volume was measured before and after soaking.

EXPERIMENT 28.—VOLUME.

Per cent. increase on 24-hour soaked volume.

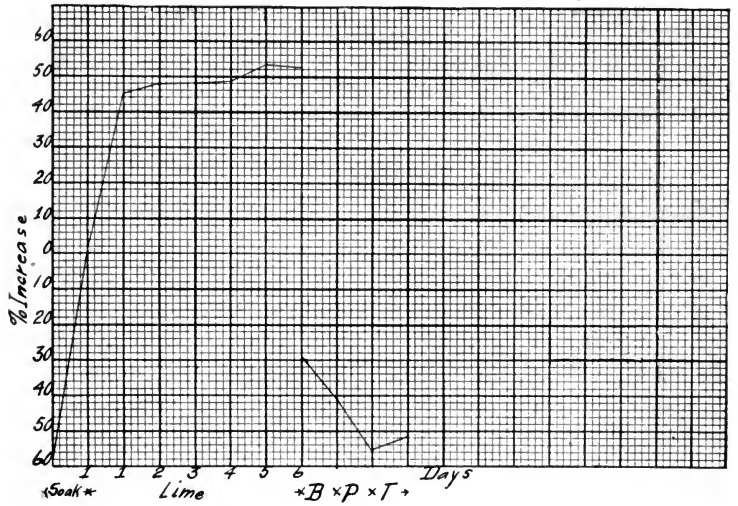


EXPERIMENT 28.—DENSITY.



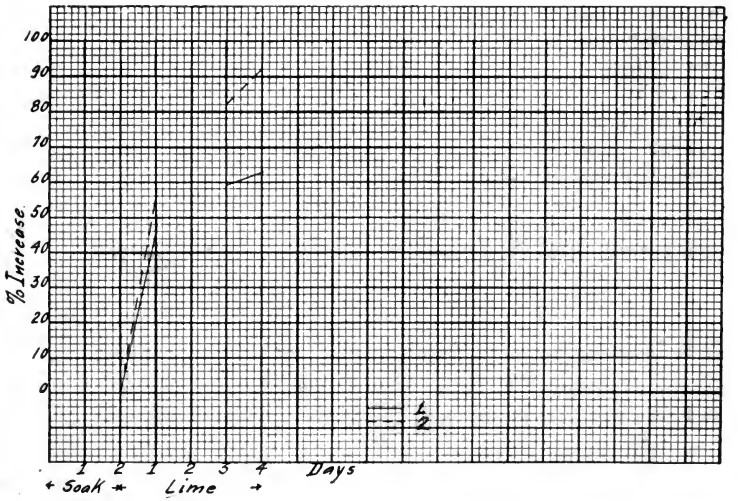
EXPERIMENT 28.—WEIGHT.

Per cent. increase on 24-hour soaked weight.



EXPERIMENT 29.—VOLUME.

Per cent. increase on 48-hour soaked volume.



EXPERIMENT S-33.—CHANGES IN VOLUME OF FLANK AND BUTT DURING SOAKING.

	Number I, butt			Number II, flank	
Condition of the skin	Volume in cc.	Per cent. increase	Condition of the skin	Volume in cc.	Per cent. increase
Dry salted	60.4	—	Dry salted	56.2	—
After 24 hours in water	75.4	25	After 24 hours in water	81.2	45

EXPERIMENT S-39B.

This experiment was made to confirm the results of Experiment S-29. Two pieces of dry salted calfskin were soaked for 48 hours in water, which was changed every 12 hours. The pieces were limed in a solution of 5 grams of lime in 400 cc. of water, for 5 days. They were unhaired and fleshed, bated with lactic acid, pickled with sulphuric and salt, and chrome tanned in the same manner as stated in Experiment S-28. One piece was from the butt, No. 1, the other, No. 2, was from the flank. Volume measurements were taken daily and the results tabulated.

EXPERIMENT S-39B CHANGES OF VOLUME OF BUTT AND FLANK.

	Number I, butt			Number II, flank		
Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase
Dry salted	45.3	—31.1	—40.7	45.3	—42.5	—48.5
In water 24 hours	72.8	— 3.6	— 4.1	84.4	— 3.4	— 3.9
In water 48 hours	76.4	0.0	0.0	87.8	0.0	0.0
In lime 24 hours	103.8	27.4	35.8	117.5	29.7	33.8
In lime 48 hours	110.2	33.8	44.2	125.9	38.1	43.4
In lime 96 hours	119.1	42.7	55.9	143.2	55.4	63.1
In lime 120 hours	122.5	46.1	60.3	150.2	62.4	71.1
Unhaired and fleshed	61.3	—15.1	—19.8	81.3	— 6.5	— 7.4
Bated	51.8	—24.6	—32.2	68.8	—19.0	—21.6
Pickled	42.0	—34.4	—45.0	52.5	—35.3	—40.2
Chrome tanned	51.5	—24.9	—32.6	62.7	—25.1	—28.6

EXPERIMENT S-39.

This is in general a duplicate of Experiment S-25. Three pieces of dry salted calfskin were limed in a solution of 5 grams of slaked lime in 400 cc. as in previous experiments, and volume and weight measurements made daily. The results follow in table, Experiment S-39. The increase and percentage increase in weight and volume are computed on the weight and volume of the skin after 48 hours soaking in water, respectively.

EXPERIMENT S-39.—CHANGES IN VOLUME, WEIGHT AND DENSITY OF SHOULDER.

Number I.

Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in g.	Increase in g.	Per cent. increase	Density
Dry salted.....	150.6	—107.7	—41.7	—	—	—	
In water 24 hours.	253.0	—5.3	—2.1	—	—	—	
In water 48 hours.	258.3	0.0	0.0	287	0.0	0.0	1.11
In lime 24 hours..	346.0	87.7	34.0	384	97.0	33.8	1.11
In lime 48 hours..	380.5	122.2	47.3	418	131	45.6	1.10
In lime 72 hours..	422.0	163.7	63.1	455	168	58.5	1.08
In lime 96 hours..	440.0	181.7	70.4	475	188	65.5	1.08
In lime 120 hours.	416.5	158.2	61.3	449	162	56.5	1.08
In lime 144 hours.	429.0	170.7	66.1	472	185	64.5	1.10
In lime 168 hours.	421.0	162.7	63.0	444	157	54.7	1.08
Unhaired and fleshed.....	236.8	—21.5	—8.3	256	—31	—10.8	—1.08

CHANGES IN VOLUME, WEIGHT AND DENSITY OF FLANK.

Number II.

Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in g.	Increase in g.	Per cent. increase	Density
Dry salted.....	105.9	—122.2	—53.5	—	—	—	—
In water 24 hours.	221.1	— 7.0	— 3.1	—	—	—	—
In water 48 hours.	228.1	0.0	0.0	252	0.0	0.0	1.11
In lime 24 hours..	324.0	95.9	42.0	357	105	41.7	1.10
In lime 48 hours..	359.5	131.4	57.4	395	143	56.7	1.10
In lime 72 hours..	375.0	146.9	64.4	412	160	63.5	1.10
In lime 96 hours..	410.0	181.9	79.7	430	178	70.6	1.05
In lime 120 hours.	432.0	203.9	89.4	469	217	86.1	1.09
In lime 144 hours.	395.0	166.9	73.1	435	183	72.6	1.10
In lime 168 hours.	369.5	141.4	62.0	403	151	59.9	1.09
Unhaired and fleshed.....	226.5	— 1.6	— 0.7	245	—7.0	—2.8	1.08

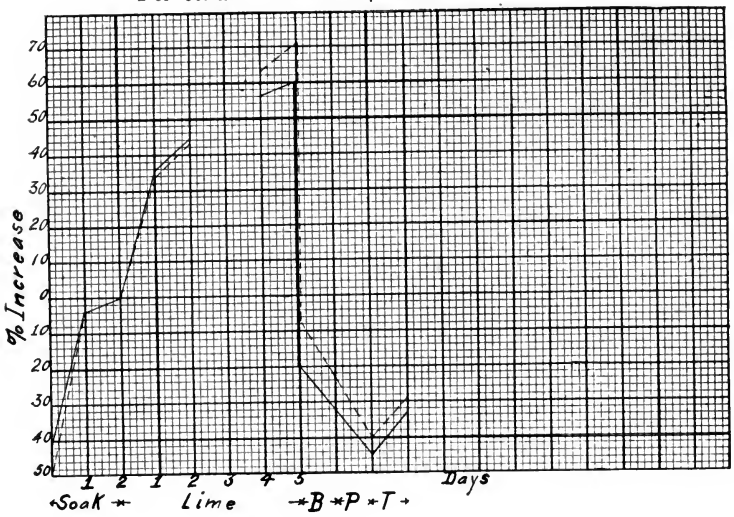
CHANGES IN VOLUME, WEIGHT AND DENSITY OF BUTT.

Number III.

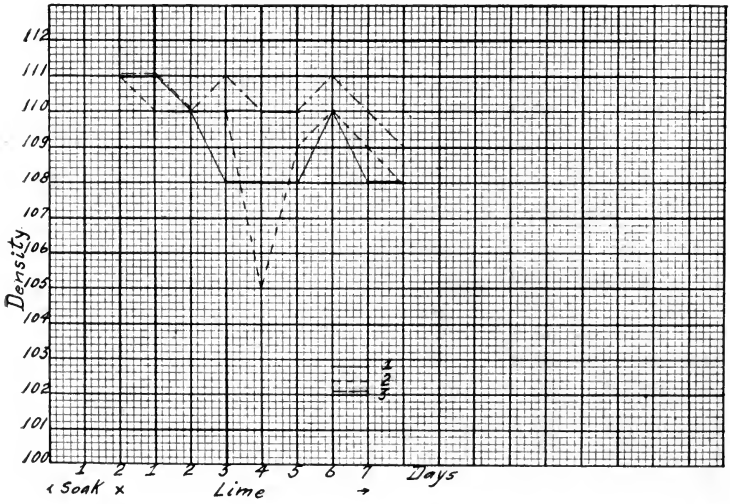
Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in g.	Increase in g.	Per cent. increase	Density
Dry salted.....	86.0	—111.7	—56.5	—	—	—	—
In water 24 hours.	183.8	— 13.9	— 7.0	—	—	—	—
In water 48 hours.	197.7	0.0	0.0	219	0.0	0.0	1.11
In lime 24 hours..	255.0	57.3	29.0	284	65	29.7	1.11
In lime 48 hours..	292.0	94.3	47.6	322	103	47.0	1.10
In lime 72 hours..	300.0	102.3	51.8	334	115	52.5	1.11
In lime 96 hours..	318.0	120.3	60.9	349	130	59.3	1.10
In lime 120 hours.	325.0	127.3	64.4	357	138	63.0	1.10
In lime 144 hours.	327.5	129.8	65.7	362	143	65.5	1.11
In lime 168 hours.	296.0	98.3	49.7	325	106	48.4	1.10
Unhaired and fleshed.....	216.0	18.3	9.3	235	16	7.3	1.09

EXPERIMENT 39-B.—VOLUME.

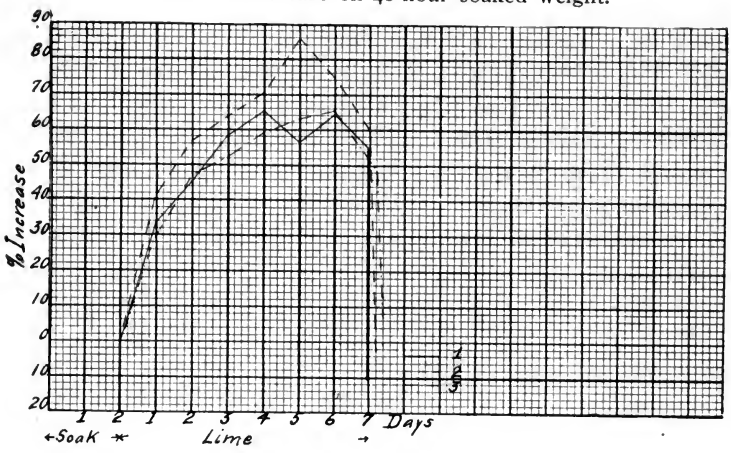
Per cent. increase on 48-hour soaked volume.



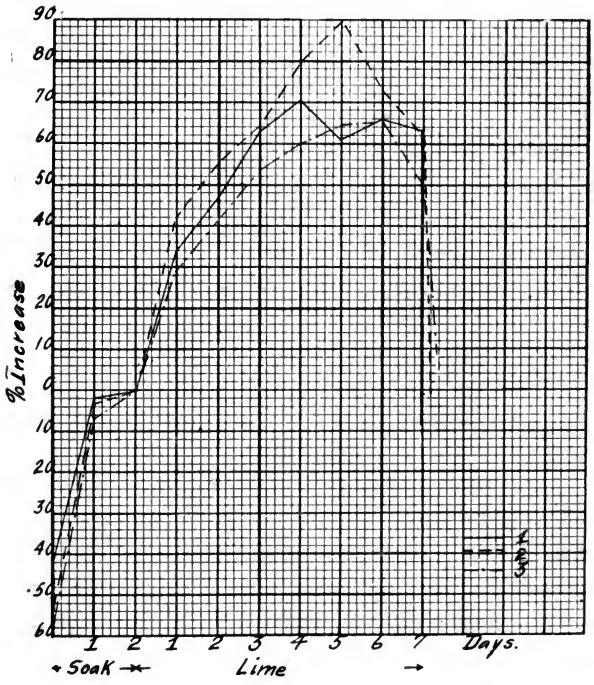
EXPERIMENT 39.—DENSITY.



EXPERIMENT 39.—WEIGHT.
Per cent. increase on 48-hour soaked weight.



EXPERIMENT 39.—VOLUME.
Per cent. increase on 48-hour soaked volume.



Attempts to Prevent Thinness of Flank.

In looking for some remedy for the excessive swelling and subsequent looseness of the flank, the following experiments were made. The reasoning was that the flank was thinner than the rest of the skin and hence had lost more inter-fibrillar substance by solution. If the flank could be protected in some manner this would be partially prevented and the resulting leather should not have so thin and flabby a flank. Some substance had to be used which was easily applied and relatively pliable. The use of aluminum soap was suggested and it was tried. The hides were painted with a hot 10 per cent. solution of aluminum sulphate and left a few minutes. Then the hides were painted with a hot 10 per cent. solution of ivory soap. The pieces were then limed in the usual manner. The results of various experiments follow.

Experiment S-31.—Two pieces of calfskin which had been soaked 24 hours in water were painted thickly with a hot 10 per cent. solution of aluminum sulphate. One of these pieces was immediately placed in milk of lime, the other, after standing 10 minutes, was painted thickly with a hot 10 per cent. solution of ivory soap. A third piece was limed 24 hours, washed thoroughly in water, painted with a hot 10 per cent. soap solution and finally returned to the limes. All three pieces gave the same result so far as could be detected by the ordinary methods of testing the quality of leather. The hair slipped just as easily as in the ordinary cases and the flank was neither fuller nor firmer. The results were negative.

Experiment S-34.—Two pieces of calfskin were taken after 24 hours soaking in water. One was soaped completely three times and then painted three times with an aluminum sulphate solution. The other was soaped and painted once on the flank only. These pieces were limed as usual and sent to the tannery to be chrome tanned and finished. All three pieces apparently gave the same result. No appreciable differences were noticed. The hair slipped just as readily as though the pieces had been limed in the ordinary manner. The leather appeared to have a better grain, but subsequent tests failed to confirm this conclusion.

Experiment S-35.—Eight pieces, which had been soaked 24 hours in water, were painted and soaped, four completely and

four only on the flank. They were then limed and tanned. After tanning the tests showed negative results. It was impossible to tell by inspection the soaped from the unsoaped area nor did any of the pieces differ apparently from normally limed and tanned skins.

The above experiments were all repeated using a 10 per cent. soap solution only. The moment the hides entered the limes a lime soap was formed. The results of these experiments were almost identical with the previous ones.

The process was studied more quantitatively in Experiment S-36, where in order to study the protective action of soap on various parts of the hide a dry salted calfskin was split down the backbone into two pieces, each of which was again cut at right angles to the backbone into three portions. The pieces on the left side were number 1, 2 and 3 starting at the shoulder and those of the right side, 4, 5 and 6 respectively. The object was to note the various increases in volume and changes in structure occurring in the process. Sections were cut parallel to and at right angles to the backbone, after 48 hours soak, after 96 hours liming and just after removing from the limes. The pieces were cut in each case from a piece of skin taken from the backbone edge and the flank edge of the sample. The samples were subjected to various treatments as follows:

No. 1.—Limed 168 hours in the regular manner.

No. 2.—Limed 144 hours, until flank unhaired easily, but butt not so readily.

No. 3.—Limed 196 hours, 2 days over-limed.

No. 4.—Soaped (10 per cent. solution) all over and limed normally 168 hours.

No. 5.—Soaped flank only and limed normally 168 hours.

No. 6.—Soaped all over and over-limed 2 days, 196 hours in all.

The sections showed that the flank was decidedly of a looser structure than the rest of the skin. The loose structure was noted in the very beginning of the process and the soap treatment apparently failed to remedy this defect. Even if the lime soap formed should hinder further action of the lime, it could not change the existing loose structure into a compact one. The

EXPERIMENT S-36—CHANGES IN VOLUME.

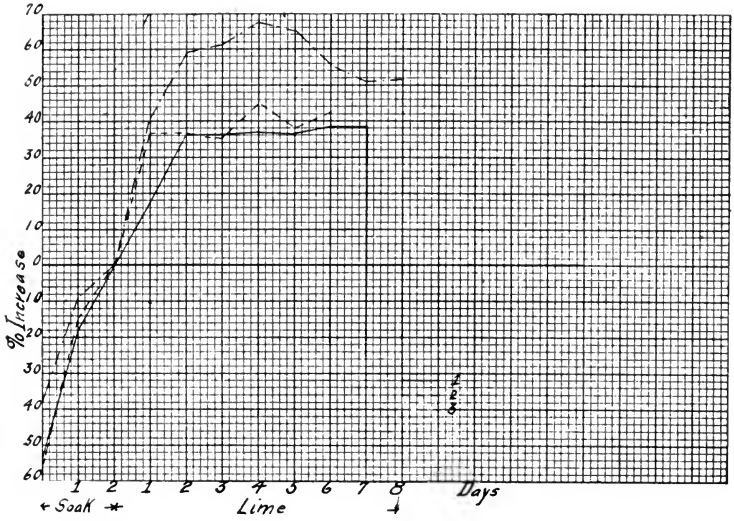
Condition of the skin	Number I			Number II			Number III		
	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase
Dry salted	40.9	—47.3	—53.5	45.1	—56.0	—55.3	71.5	—44.4	—38.2
In water 24 hours	72.2	—16.0	—18.1	85.4	—15.7	—15.5	106.0	—9.9	—8.6
In water 48 hours	88.2	0.0	0.0	101.1	0.0	0.0	115.9	0.0	0.0
In lime 48 hours.....	103.5	15.3	17.3	137.8	36.7	36.3	163.7	47.8	41.2
In lime 24 hours.....	119.9	31.7	35.9	137.9	36.8	36.4	184.4	68.5	59.1
In lime 72 hours.....	120.1	31.9	36.2	137.2	36.1	35.6	187	71.1	61.4
In lime 96 hours.....	120.5	32.3	36.6	146.5	45.4	44.8	194.4	78.5	67.7
In lime 120 hours.....	120.2	32.0	36.3	139.2	38.1	37.6	190.8	74.9	64.6
In lime 144 hours.....	121.9	33.7	38.2	144	42.9	42.4	180.6	64.7	55.8
In lime 168 hours.....	121.9	33.7	38.2	—	—	—	174.7	58.8	50.7
In lime 192 hours.....	—	—	—	—	—	—	175.8	59.9	51.6
Unhaired and fleshed ..	66.1	—22.1	—25.0	79.2	—21.9	—21.6	93.	—22.9	—19.8

EXPERIMENT S-36—CHANGES IN VOLUME.—(*Continued.*)

Condition of the skin	Number IV			Number V			Number VI		
	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase
Dry salted	43.3	—34.0	—44.0	63.1	—37.3	—37.1	70.6	—46.5	—39.6
In water 24 hours	69.8	—7.5	—9.7	96.3	—4.1	—4.1	113.0	—4.1	—3.5
In water 48 hours	77.3	0.0	0.0	100.4	0.0	0.0	117.1	0.0	0.0
In lime 24 hours	177.8	46.5	52.4	148.5	48.1	47.9	193.9	76.8	65.5
In lime 48 hours	122.1	44.8	58.0	162.7	62.3	62.0	202.9	85.8	73.2
In lime 72 hours	126.3	49.0	63.5	173.9	73.5	73.1	208.9	91.8	78.3
In lime 96 hours	126.6	49.3	63.8	179.3	78.9	78.5	220.0	102.9	87.7
In lime 120 hours	132.4	55.1	71.4	181.1	80.7	80.3	212.6	95.5	81.5
In lime 144 hours	122.4	45.1	58.4	161.1	60.7	60.4	183.1	66.0	56.3
In lime 168 hours	125.7	48.4	62.5	177.0	76.6	76.3	196.7	79.6	68.0
In lime 192 hours	—	—	—	—	—	—	172.7	55.6	47.5
Unhaired and fleshed	61.0	—16.3	—21.1	78.3	—22.1	—22.0	100.8	—16.3	—13.9

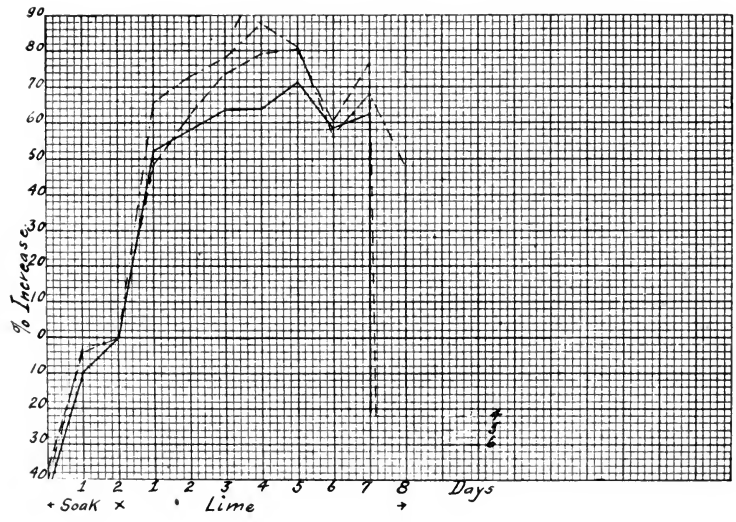
EXPERIMENT 36.—VOLUME.

Per cent. increase on 48-hour soaked volume.



EXPERIMENT 36.—VOLUME.

Per cent. increase on 48-hour soaked volume.



samples were all unhaired, fleshed, bated, pickled and chrome tanned and pronounced fair leather. The grain in all samples was good and showed that the soap treatment caused no apparent harm. The volume measurements are given in table, Experiment S-36, and are shown also in curves.

Some attempts were made to fill the flank so that it would be as full as the rest of the skin. The hides after depilation were suspended in 1, 2, 5 and 10 per cent. solutions of glue and a few cubic centimeters of methylene blue were added. The dye showed the extent of penetration of the solution. After the usual chrome tannage, the results obtained were unsatisfactory. Some flanks appeared to have been improved and others were as if they had not been treated with glue. Then 1, 2, 5 and 10 per cent. gelatine solutions were tried. The results were practically the same as before. In both cases the finishing of the leather was attended by difficulties. Some pieces took too great a gloss and others remained too dull. In the next series fresh blood and glue, blood and gelatine were used. About 50 per cent. of blood and 50 per cent. of a 10 per cent. solution of glue or gelatine were used. Although great care was taken to watch the hides carefully, many were destroyed by bacteria. Even the addition of germicides, such as mercuric chloride and phenol failed to take care of the putrefactive bacteria. So long as bacterial limes are used this process will be attended with very great difficulties and can hardly be made commercial.

Some experiments were tried on pickled stock using glue and gelatine to fill the flanks. The results did not justify the continuation of work along these lines.

The greatest dfficulty in experiments of this kind is that the judgment of an expert is required to determine improvements. Moreover, improvements of a commercial value must be noticeable not only to an expert but also to the layman.

Results of Studies of Changes in Weight, Volume and Area of Calfskin During the Tanning Process.

The results of these tests can best be studied from the curves which are computed to a common basis of percentage change from the condition existing when the skin entered the limes.

Measurements of change in superficial area were made in Experiments 26 and 28 and are given in detail in the tables.

The dry salted skins expanded 27.1 and 19.4 per cent. respectively in area during the soaking process but both remained relatively constant in area throughout the subsequent operations of liming, bating and pickling. No. 28 showed a considerable increase after unhairing but this mechanical stretching disappeared in the pickle. Through an oversight the area of the wet tanned skin was not determined in Experiment 26 and the area for the dried finished leather while about 5 per cent. greater than that of the dry salted skin, has little significance on account of the impossibility of standardizing the amount of stretching the leather received in the drying process. The leather of S-28 measured wet showed a shrinkage in area of about 10 per cent. compared with the pickled stock and an increase in area of about 12 per cent. compared with the dry skin.

A comparison of the weight and volume curves of all experiments shows great general similarity. Both volume and weight increase in approximately the same ratio during the soaking and liming process. The increase is rapid during the first 24 hours in water and slower after that time. On putting into lime the increase is again very rapid during the first 24 hours and becomes slower thereafter, reaching a maximum after about 5 days in lime. These limes were all bacterial but did not contain added sulphides.

The increase in volume of different pieces varies from 40 to 80 per cent. The experiments on changes in area quoted above show that very little change took place after the skin was soaked. These changes in volume are therefore an almost direct measurement of changes in thickness. This increase in volume and hence approximately of thickness runs up to a maximum of 90 per cent. over that of the soaked hide. The least total increase in volume shown by any skin is 38 per cent. over that of the soaked hide.

Marked differences exist between different portions of the same skin limed in the same solution. In each Experiment 25, 36 and 39 a half calfskin was trimmed and cut at right angles to the backbone into three pieces of approximately equal size. These three pieces were carried through the whole operation together.

The differences in the maximum amount of swelling of these three skins during the liming process is as follows:

	Shoulder Per cent.	Middle Per cent.	Rump Per cent.
Experiment 25.....	51	40	62
Experiment 36.....	72	80	88
Experiment 39.....	70	90	65

No conclusions can be drawn except that different portions of a dry salted skin may swell very differently in the limes. This may be due to differences in thickness, in structure, in amount of fat or to other causes and is discussed somewhat later.

While the curves show that the changes in volume and weight are in general similar, the exact relationship is shown in a very similar manner by the curves of density. Tests 25, 26, 27, 28 and 39 are available for a study of this relationship. Any errors of measurement are magnified in this method of treatment and as is to be expected the curves are not altogether consistent. Certain general features are, however, clearly recognizable. The density decreases on soaking in water, but usually increases or stays constant during the first 24 hours in limes. It then decreases as the liming process proceeds and reaches a maximum after 96 hours in the limes. It then rises to a distinct maximum after 144 hours in lime but usually falls again within the next day or two. The density falls again in the bating process whether a bran drench or lactic acid be used and rises sharply in the pickle to fall again somewhat in the wet tanned leather.

The changes are in general those which would be expected when a material heavier than water absorbs water and swells. The volume increases more rapidly than the weight. The same phenomenon persists in the limes. The sharp change in the curve while still in the limes is unexpected but may be in some way connected with bacterial action. The immersion in the feebly acid bath swells the hide more rapidly than the weight increases and hence the density falls again. The pickle shrinks the skin and brings its density back to a figure nearly that of the dry skin.

The most noticeable defect in calfskins is the flabbiness of the flank. Microscopic examination showed this part of the skin to be of loose structure and thinner than the rest. The relative swelling of butt and flank was tested in Experiments 29, 33 and

39B. In every case the flank swelled more than the butt, the figures for maximum increase in volume on 24 hours soaking over the dry volume being:

	Butt Per cent.	Flank Per cent.
Experiment 33	25	45
Experiment 39B	61	86

The maximum swelling in lime referred to the volume after soaking 48 hours was:

	Butt Per cent.	Flank Per cent.
Experiment 29	63	92
Experiment 39B	60	71

The effect of coating the flesh side of a calfskin with lime soap at the time of its immersion in the limes is shown in the table and the two sets of curves in Experiment 36. The soaped pieces all swelled decidedly more than the unsoaped. The maximum swelling expressed in percentage increase on the wet volume is as follows:

	Not soaped	Soaped
Shoulder	38	72
Middle	45	81
Rump	68	88

The volumes of the soaped pieces decrease more after unhairing and fleshing than do those of the unsoaped, so that the effect of the soap seems to be lost. Volume measurements were discontinued after this point and therefore quantitative figures on the finished leather are not available. However, the pieces which had been soaped before liming seemed slightly fuller.

Study of Depilation in Sterile Limes—Review of Literature.

Although the bacteria of bating and puering have been studied quite thoroughly, those of the limes have been more neglected. While certain agents have been known for some time, which without the aid of bacteria, were able to depilate a hide, still in the ordinary processes used in practice, the presence of bacteria was not only taken for granted, but if through any reason bacteria were absent active cultures were always added. This idea has had so firm a hold that, whenever a new tannery was

established some old lime from another tannery was conveyed to the new lime pits in order to "start," that is inoculate them.

The idea that a solution of lime could, under sterile conditions, cause loosening of the hair so that a hide could be unhaired easily, was considered impracticable. Parker[13] states, "Formerly it was believed that the lime swelled the fibers of the hide, dissolving the hair bulb or root and loosening the epidermis, thus rendering the removal of the hair easy; but the liming process is now known to be both chemical and physical, the loosening of the hair being largely due to the action of enzymes and the products of bacteriological action. Hides cannot be unhaired by sterile limes, so that the process of Payne and Pullman,[14] by which the hides were first soaked in caustic soda and afterward in calcium chloride, so as to form lime within the fibers, was unworkable unless preceded by the soaking of the hides in a foul soak to obtain the necessary bacteriological action." He also states,[15] "It was fully realized that bacteriological action played an important part in the unhairing and that the action of old limes was largely bacterial and that hides could not be unhaired from a sterilized lime." Procter[16] believed that bacteria were essential in the liming process. Stiasny[17] states that the liming process is both a chemical and bacteriological one. Villon in his "Traite de la Fabrication des cuirs" discusses the liming and sweating processes. He states positively[18] "L'echauffe est une fermentation particuliere causee par un microbe determine. L'epilage a la chaux est cause par la meme fermentation. Que la peau ne se depile pas en presence de la chaux apres sterilization." He states that the unhairing of skins is due to the action of definite bacteria and that sterilized lime will not cause unhairing of a hide. He sterilized his samples of hide by means of dry heat. He subjected the samples to 50° C. for 24 hours and then 110° C. for 10 minutes. Schmitz-Dumont[19] has shown that not all the bacteria present were killed by this treatment.

[13] *Jour. Soc. Chem. Ind.* Vol. 29, p. (1912 910).
[14] English patent, No. 2,873.
[15] *Jour. Soc. Chem. Ind.* Vol. 31, p. 371 (1912).
[16] *Prin. of Leather Mfg.* pp. 135, 137.
[17] *Leather Trades Rev.* July 2, 1913.
[18] *Villon Traite de la Fabrication des cuirs*, p. 487.
[19] *Ding. Polyt. Jour.* Vol. 300, p. 140.

Von Schroeder[20] made many experiments along the above lines, and as his conclusions are different, his work will be given more fully. His methods were as follows: Hides were obtained from a tannery, washed 3 days in water, then placed in a saturated salt solution. The salt solution was changed until the hide no longer absorbed salt. The hides were kept in this salt solution and were considered sterile. The lime used was sterilized in the following manner: The lime solutions were placed in flasks around the neck of which cotton moistened with salicylic acid had been wound so that the whole could be covered with a Petri dish. These flasks were placed in a water bath up to 1 inch from the top of the neck in water. The bath was then heated to boiling and kept boiling ½ hour. This treatment was repeated on 3 successive days. This lime solution, was then called sterile. In order to observe the action of sterile water on hides, several flasks of water were treated precisely like the lime solutions. The sterile hides were placed in the sterile lime and sterile water flasks June 29th. On July 4th, a sample was taken from a water and a lime flask. No odor was perceptible in either case. The hair could be removed with great difficulty and in fact it was almost impossible to get it off. One cubic centimeter of the water and one of the lime solution were now transplanted into 10 cc. of gelatine. All these sub-cultures gave a positive result, that is a growth of bacteria or molds, whereas if the solution had been really sterile there should have been no growths. On July 11th a flask of each kind was again opened. The hair slipped easily. Again all sub-cultures made gave positive results. On August 3rd the remaining flasks were opened and all sub-cultures again gave positive results. Moreover, the solutions all had a putrid odor.

Van Schroeder then took part of the water in the flasks, added it to some sterile limes and the sub-cultures made showed few colonies. His conclusion was that the lime killed the bacteria contained in the water. His final conclusion based on this last experiment was that in the limes, unhairing takes place without bacterial action in a short time, but that in pure (reinem) water only after bacteria have developed and produced ammonia enough to make the solution alkaline. His second series was as

[20] *Ding. Polyt. Jour.* Vol. 301, pp. 65, 90.

follows: The hides from the saturated salt solution were placed in 99 per cent. alcohol which was renewed every day for 4 days. These hides were considered sterile. The flasks containing water and lime water solutions were sterilized as before. All except one of the sub-cultures taken after 4 days gave positive results. In this case some hairs were transplanted to gelatine by means of a forceps sterilized in a flame. There is a possibility that the forceps was too hot and killed the bacteria, or that the melted gelatine was too warm. After 6 days two more flasks were opened and sub-cultures made. All but two gave positive results. These two sub-cultures were made by transplanting 0.1 cc. and 0.01 cc. of the lime solution in 10 cc. of gelatine. The final conclusion drawn from these experiments was that "Die Vorbereitung der Haut zum Enthaaren durch den Aescher process von Bakterien überhaupt unabhangig und nur eine Wirkung der alkalischen Reaction des Kalkes ist." Von Schroeder then assumes that Villon's idea that *bacillus pilline* must be present in limes in order that the hair be loosened, is no longer true. Unfortunately Von Schroeder died before the work was completed and the paper was published by others. The results do not bear out the assumption that the hides and solution used were really sterile. On the contrary all but two sub-cultures from the supposedly sterile solutions gave positive results. The sub-cultures which were negative under aerobic condtions were not duplicated under anaerobic conditions. There is no valid reason why anaerobic bacteria could not have been present. He also neglected to guard against the inhibiting action of the lime. He showed at great length that the lime solution killed, or rather to be accurate inhibited the growth of bacteria obtained from the infected water used in the first experiment. Afterward he did not take this fact into consideration, but transplanted his solution from the lime flasks into the same amount of gelatine—10 cc. as in the experiment using water only.

Griffith[21] made several experiments on a sterile liming process using carbon bisulphide and phenol as disinfectants. He does not give any data nor information about the actual methods used or precautions taken to prevent infection of the solutions but merely speaks of "pieces of hide previously sterilized with carbon bisul-

[21] JOURNAL Amer. Leather Chem. Asso., Vol 5, p.115 (1910).

phide and with phenol and the liming carried out in sealed jars. The carbon bisulphide hide unhaired in 24 days and the phenol hide unhaired in 18 days and an experienced bacteriologist was unable to discover the presence of bacteria. Von Schroeder experimented with fresh salted hides under sterile conditions and he was unable to discover that the absence of bacteria influenced the activity of the lime as a depilatory." The above statements would have been more convincing if the methods of bacteriological control had been given more fully. Griffith concedes that Von Schroeder's work was correct and he admits that the latter worked under sterile conditions. As was pointed out before this was not the case. Von Schroeder never had sterile conditions prevailing in any of his experiments as his sub-cultures always showed bacteria or molds. Griffith relied entirely on carbon bisulphide as a sterilizing agent. Carbon bisulphide may be an antiseptic agent but it is not a disinfectant for it does not kill all organisms, as was shown by Procter.[22]

The experiment with carbon bisulphide gave approximately the same results as that with phenol. This may have been due to the fact that under the conditions existing during the experiment the carbon bisulphide was present in sufficient quantity to prevent a noticeable increase in the number of bacteria present. The above experiments cannot be accepted as accurate in the scientific sense.

Experimental Work on Sterilization of Hides.

The following experiments were planned to settle definitely whether bacteria were necessary in the depilation process. The sterilization of hides offered the first difficulty. After reading of various methods[23] using sulphur dioxide, phenol, etc., the Seymour-Jones method was finally adopted as offering the best chances of success. The method consists of immersion of the hide for 24 hours in a 0.02 per cent. solution of mercuric chloride and a 0.5 per cent. solution of formic acid.

In order to test Seymour-Jones method of sterilization for its effectiveness as a sterilizing agent the following experiments were made. Samples of hide about 1 x 2 centimeters were soaked in

[22] Procter, Principles of Leather Manufacture, p. 135.

[23] Journal Amer. Leather Chem. Asso., Vol 5, pp. 508-10.

the solution 24 hours. They were then removed with sterile forceps and washed three times by immersion, using a liter of sterile water each time. Then they were planted by means of sterile forceps into 150 cc. of sterile medium, beef tea, gelatine, agar, pea-bean medium, and litmus glucose gelatine being used. The results are shown in the table.

SEYMOUR-JONES TEST.

No.	Beef tea	Gelatine	Pea-bean	Agar	Anaerobic conditions. in a Novy jar, over hydrogen. Litmus glucose gelatine	Check for Anaerobes B. tetanus	Check Aerobes B. lactici
1....	—	—	—	—	—	+	+ + + +
2....	—	—	—	—	—	+	+ + + +
3....	—	—	—	—	—	+	+ + + +

Although these solutions all showed negative results it is necessary, before admitting the test to be conclusive, to show that the amount of mercuric chloride transferred could not have been sufficient to have inhibited the growth of bacteria in the culture media. Mercuric chloride acts as an antiseptic agent even in dilutions of 1 to 100,000. The samples after washing thoroughly in 3 liters of sterile water had very little mercuric chloride adhering. Moreover, the volume of medium used was large, 150 cc. or more in all cases. This again increases the dilution of the mercuric chloride and hence eliminates its antiseptic action.

The dilution at which formic acid still exerts its antiseptic action is not known definitely. The fact was taken into consideration, however, that the antiseptic action of formic acid is usually less than that of mercuric chloride. If one assumes the piece of hide transferred, to be all formic acid, and then takes into consideration the dilution resulting from the washing in sterile water, one will see that the dilution is more than 1 to 200,000 and that there is no chance of any antiseptic action interfering with the results. In order to check whether the medium was suitable for growing bacteria, *bacillus tetanus* and *bacillus acidi lactici* were planted under anaerobic and aerobic conditions respectively. The results were positive in all cases.

Since the checks were always positive and the sub-cultures

from the sterilized hides negative, it was therefore considered proven that the Seymour-Jones method of sterilization is effective under the given conditions of experiment.

Test for Bacteria in the Limes.

Since there might be some question as to the presence of bacteria in the limes, sub-cultures were made on agar, beef tea, pea-bean media and gelatine. All sub-cultures gave positive results.

Wood[24] has shown that bacteria of various kinds are present in the limes. Abt[25] has also proven that bacteria are present in the liming process.

The medium used in transplanting sub-cultures in all the following experiments was slightly more alkaline than that usually employed for this purpose.

Experimental Work—Laboratory Tests on Depilation.

The procedure now used was as follows: A 250 cc. Soxhlet flask, provided with a tight cotton plug was sterilized for 1 minute at 200° C. in a dry heat sterilizer. It was cooled and 175 cc. of water and 50 grams of slaked lime were added. The flask was then autoclaved at 110° C. for 20 minutes and allowed to cool. A piece of hide which had been previously sterilized in a solution (Seymour-Jones) of 1-5,000 mercuric chloride and 0.5 per cent. formic acid, for 24 hours, was added to this solution by means of sterile forceps. This flask was then examined every 2 or 3 days, great care being taken to prevent infection of its contents. After 11 days the hair could be removed with difficulty, but after 13 days the hide could be easily unhaired.

In order to prove conclusively that bacteria were absent, sub-cultures of the lime solution and of hair were made on various media under aerobic and anaerobic conditions. That the medium used was suitable for the growth of bacteria was proven by planting test organisms. For this purpose *bacillus acidi lactici* and *bacillus tetanus* were used under aerobic and anaerobic conditions, respectively. The results obtained are shown in the following table:

[24] *J. Soc. Chem. Ind.*, Vol. 29, p. 666. (1910).
[25] *Bull. Syndicat. Gen. Cuirs et Peaux*, p. 416, Nov. 10, 1908.

CHECK TEST ON STERILITY OF CONDITIONS.

	Beef tea	Gelatine	Pea-bean	Under anaerobic conditions in a Novy jar previously exhausted and hydrogen passed in. Litmus glucose gelatine
1 loop of lime solution	—	—	—	—
Hair	—	—	—	—
Checks	+	+	+	+

These results are very satisfactory and show, since all the subcultures were negative and the checks positive, that no bacteria capable of growing were present in the limes used.

After it had been shown that the Seymour-Jones method of sterilization with mercuric chloride and formic acid was reliable and preliminary tests had shown that it was possible to unhair a skin with sterile limes, the following series of tests was undertaken to study the process more quantitatively. Four different solutions were used to determine how lime alone, and lime with sulphur compounds acted. One flask contained lime only, a second lime and red arsenic sulphide, a third, lime, red arsenic sulphide and hair, and the fourth lime and hair. The solutions containing hair were boiled vigorously for 45 minutes, before use, with the idea that some hydrolysis of the hair would take place with formation of soluble sulphur compounds and amino acids and that thus the action of an old lime might be simulated. The details of the tests are as follows:

Four pieces of dried calfskin 2 x 3 inches in area were soaked 24 hours in a solution of 0.02 per cent. mercuric chloride and 0.5 per cent. formic acid. Four 250 cc. Soxhlet flasks were plugged with cotton and sterilized for 1 minute at 200° C. in a dry heat sterilizer. To one of these flasks 50 grams of lime and 175-200 cc. of water were added. To another sterile flask 50 grams of lime, 175-200 cc. of water and 1.5 grams of red arsenic sulphide were added. Then the flasks which were to contain boiled hair were prepared as follows: 200 cc. of water, 50 grams of lime and 10-12 grams of hair clipped from a calfskin, were boiled vigorously for 45 minutes. This solution was placed in a sterile flask. Then 200 cc. of water, 50 grams of lime, 1.5 grams of red arsenic sulphide and 10-12 grams of hair were boiled 45 minutes and put into the fourth sterile flask. Then the four flasks were autoclaved for 20 minutes at 110° C. A piece of

EXPERIMENT 38—CHANGES IN HIDES DURING DEPILATION IN STERILE SOLUTION.

	Number I	Number II	Number III	Number IV
Date	Lime, arsenic, sulphide and hide	Lime and hide	Lime, arsenic, sulphide, hair and hide	Lime, hair and hide
10–3	All the flasks charged.			
10–4	All flasks well shaken for	five minutes.		
10–5	10gms. sterile lime added	to Numbers II and IV.		
10–10	Hair pulled easily almost all dissolved.	No noticeable change.	Hair pulled fairly easy.	No change.
10–12	Hair nearly gone.	Hair pulls but not easily.	Hair slips very easily.	Hair slips but not as well as I, better than II. No odor noticeable.
10–19	Has odor of hydrogen sulphide.	Hair slips easily. A slight odor, not hydrogen sulphide.	Odor like urine, decomposition, no hydrogen sulphide.	
10–29	No change; still hydrogen sulphide odor.	Hair slips very easily, slight odor not hydrogen sulphide.	Same.	Same.
11–5	Slight hydrogen sulphide odor. Top layer going fast; corium firm.	Upper layer firm, no odor. Hair slips very easily.	Hide beginning to disintegrate, that is, to soften so it can be torn with tweezers. Odor same, but weaker.	No odor. Upper layer easy to remove by scraping. Corium firm, however.
11–17	Same as above.	Same. No odor. Grain not soft.	Same odor; otherwise about like Number I.	Top layer going; no odor, scum like soap on flesh side.
12–1	Upper layer still present but badly decomposed.	Same; upper layer still good.	Same, not much odor, upper layer all gone.	Upper layer still present and fairly firm.
1–12	Upper layer gone very little odor.	Upper layer attacked and soft; can be scraped off. No odor.	No odor. Flesh side badly attacked. Corium good.	Upper layer soft and practically disintegrated. Corium good.
2–6	Flesh side mushy, no odor. Corium good.	No odor. Flesh side mushy. Corium good, but somewhat softer.	No odor. Flesh side badly attacked; mushy, corium good.	Upper layer gone. Corium good. No odor. Flesh side mushy.
2–12	Flesh side going. No odor corium good about same. Can be scraped off by tweezers.	About the same, no odor.	Same, no odor.	About the same. Corium good. No odor.
3–8	No odor. Very glassy almost all gone.	No odor. Flesh side very mushy. Corium softer. Still has firm feeling. Can be scraped off.	No odor. Corium very soft glassy almost all gone. Very small piece left.	No odor. Piece still left. Flesh side very mushy swollen like scum. Grain side smooth, but scrapes easily. Lower layer still very firm.

sterile hide was now planted in each of the flasks after cooling, by means of sterile forceps.

The following table gives some of the observations made on these samples. Every time the hides were examined great care was taken to handle them with sterile instruments and in such a manner that they remained sterile. The flasks were all kept at the room temperature. They were not examined every day, for the danger of contamination would have increased at a greater rate than the notable differences in the skin. The remarks concerning the condition of the skin are rather indefinite to be sure, but the changes were very gradual and consisted in the main in such as are hard to describe accurately.

In order that there might be no question of the sterility of the various flasks, sub-cultures were made on various media after the test had been running 2 months. Gelatine, beef tea and pea-bean media were used for aerobic and litmus glucose gelatine for anaerobic experiments. *B. acidi lactici* and *B. tetanus* were used as checks respectively. The results follow in the table.

EXPERIMENT 38.—CHECK ON STERILITY OF SOLUTIONS.

Number of flask	I	II	III	IV	
Gelatine plates	—	—	—	—	Planted 2-12-14
Gelatine tubes	—	+*	—	—	Examined daily from
Pea-bean tubes	—	—	—	—	2-12 to 2-24
Beef tea tubes	—	—	—	—	
Checks	+	+	+	+	
Anaerobic conditions in Novy jar over hydrogen	—	—	—	—	
Litmus glucose gelatine					Planted 2-12-14
Checks	+	+	+	+	Examined 2-26-14

* One positive result out of eight gelatine tubes.

It will be noted that all the results are negative with the exception of one of the eight gelatine tubes planted from Flask II. To study this organism further it was transplanted and plated. It proved to be a streptococcus, white, liquefying gelatine and was probably Matschek's white streptococcus. Then six more gelatine sub-cultures were made from the original flask. All were negative. Therefore, it is reasonable to presume that this one tube became infected through air and technique. The anaerobes were transplanted to litmus glucose gelatine and placed in a Novy jar. This was exhausted to 28.8 millimeters vacuum, then hydrogen was passed in. This process was repeated three times then the jar was closed and left for 14 days. No

growths were noticeable. Tetanus bacillus was used as a check and gave a good growth in litmus glucose gelatine to which one loopful of sterile lime water had been added. In the case of aerobes, the check used on gelatine with one loopful of sterile lime was *bacillus acidi lactici.* In all cases the effect of the lime and water which was unavoidably conveyed by the platinum loop during inoculation, and which might have had an antiseptic or germicidal action, was provided for by using a large amount of medium at least 15 cc. in each case and to be more certain, for each set one flask containing 100-150 cc. of medium was used.

This Experiment 38 was continued 5 months as shown by the table and at the end of the period, the flasks were again tested. All tubes and flasks showed negative results, that is no growths. The checks were all positive showing that conditions were favorable for the growth of bacteria. Details are given in the following table:

EXPERIMENT 38.—FINAL CHECK ON STERILITY OF SOLUTIONS.

Number of flask	I	II	III	IV	
Gelatine plates	—	—	—	—	Planted 3-8-14 examined daily from
Gelatine tubes	—	—	—	—	3-9 to 3-23
Pea-bean	—	—	—	—	
Beef tea	—	—	—	—	
Checks	+	+	+	+	
Anaerobic conditions Litmus glucose gelatine	—	—	—	—	Planted 3-8-14 Examined after 14 days
Check	+	+	+	+	

EXPERIMENT 40.

This experiment was made both to check results of the previous one and to see whether the presence of hair had any marked effect on the changes taking place during the sterile liming. The samples of hide were sterilized 24 hours in Seymour-Jones solution then transferred with sterile forceps to sterile flasks containing lime, and lime and arsenic sulphide. The samples were in one case hide which had had the hair closely clipped off before sterilization and in the other case normal hides with hair on. At the same time 20 grams of hair were sterilized 3 days and then placed in 600 cc. of water containing 50 grams of lime with the idea in mind of noting changes on pure hair under said conditions. The results follow in the table. Sub-cultures were made from all flasks on various media precisely as in the previous tests. The results were all negative and are shown in the following tables:

EXPERIMENT 40—CHANGES IN HIDES DURING DEPILATION IN STERILE SOLUTIONS.

Date	Number I Shaved 5 grams lime 0.15 gram AS_2S_3 400 cc. water	Number II Hair on Same as Number I	Number III Shaved 5 grams of lime 400 cc. water	Number IV Hair on Same as Number III	Number V Hair 20 grams 50 grams lime 600 cc. water
12–3	Into all solutions after 24	hours sterilization in Sey-	mour-Jones solution.		Hair sterilized 3 days.
12–6	No change.	Hair slips very little when pulled strongly.	No change, no odor.	No change, no odor.	No change.
12–7	" "	Same.	No change, no odor.	" " " "	" "
12–8	" "	"	" " " "	" " " "	" "
12–9	Hair slips some, that is, comes off on scraping.	Hair slips more easily. Slight odor of hydrogen sulphide.	" " " "	Hair tight, can be pulled; slight odor.	No odor. No change.
12–13	Hair can be scraped easily. Very slight odor epidermis attacked.	Hair slips very easily; much of it dissolved. Epidermis attacked; slight hydrogen sulphide odor.	" " " "	Hair still tight, not much if any odor.	Same.
12–20	Not much odor, may be slight hydrogen sulphide. Upper layer badly attacked. Hair all gone. Corium still hard and firm.	Hair nearly all gone, upper layer mushy. Corium good, odor of hydrogen sulphide.	May be slight odor, hard to tell. Hair can be scraped easily. Corium good and harder than Numbers I and II.	Hair slips fairly easy. Corium hard like Number III. Flesh side somewhat swollen. Very little odor if any.	Slight odor of hydrogen sulphide.
1–5	Upper layer badly attacked. Corium firm and hard. Very little odor.	Not much odor of hydrogen sulphide. Upper layer more attacked than Number I. Patches of it gone.	Upper layer not soft like I and II. No odor.	Hair slips very easily. Upper layer attacked, it can be scraped off. No odor.	Same.
1–8	About same. No odor, same. Upper layer very mushy. No odor corium firm. Flesh side swollen.	About same. No odor, same. Upper layer almost all gone. No odor. Corium good. Not so firm.	Same. Corium firm, same. No odor. Upper layer still good. Slightly attacked corium good and firm.	Same. Same, corium good.	About the same. Slight odor of ammonia and hydrogen sulphide.

EXPERIMENT 40—CHANGES IN HIDES DURING DEPILATION IN STERILE SOLUTIONS.—(*Continued.*)

Date	Number I Shaved 5 grams lime 0.15 gram AS_2S_3 400 cc. water	Number II Hair on Same as Number I	Number III Shaved 5 grams of lime 400 cc. water	Number IV Hair on Same as Number III	Number V Hair 20 grams 50 grams lime 500 cc. water
2–1	Upper layer gone in patches. Very mushy. Corium still firm. No odor.	Upper layer gone. No odor. Corium firm.	Upper layer mushy. No odor. Corium firm.	Upper layer almost all gone. Corium good. No odor.	Hair mushy. Same, hair mushy, some dissolved.
2–12	Upper layer all gone. Corium firm. No odor.	No odor. Corium firm. Slightly softer. Flesh side slightly swollen.	Upper layer partly gone. Corium better than I and II. No odor.	Upper layer practically gone. No odor. Corium good as Number III.	About the same, more hair dissolved.
2–25	Corium firm, no odor. Flesh side softer.	Corium firm, no odor. Flesh side softer.	Flesh side swollen a little. No odor. Corium good.	Flesh side swollen, no odor. Corium firm and good.	Stronger odor of ammonia, less odor of hydrogen sulphide.
3–2	Flesh side getting softer and swollen. Corium good not so firm. No odor.	Flesh side getting mushy. More swollen. Corium getting softer. No odor.	Flesh side getting mushy. Corium good and firm. No odor.	Flesh side quite mushy and swollen no odor. Corium good. Slightly softer.	About the same. Solution has a yellowish tinge.
3–9	Very glassy, mushy. Corium very much attacked. No odor.	Very glassy, mushy corium. Odor of hydrogen sulphide. Flesh side gone.	Peels in layers. More firm than Numbers I and II. Corium glassy. Mushier on flesh side. Very little odor.	Hair not dissolved, very slight odor of hydrogen sulphide. Corium still good. Glassy, flesh side mushy. Upper layer of corium can be scraped easily.	Weaker odor of ammonia and hydrogen sulphide. Considerable hair dissolved, some colloidal substance in suspension. Solution yellow.

EXPERIMENT 40.—CHECK ON STERLITY OF SOLUTIONS AFTER TEN WEEKS.

Number of flask	I	II	III	IV	
Gelatine plates	—	—	—	—	Planted 2–12 examined
Gelatine tubes	—	—	—	—	Daily from 2–12 to 2–24
Beef tea tubes	—	—	—	—	
Pea-bean tubes	—	—	—	—	
Checks	+	+	+	+	
Anaerobic conditions. Litmus glucose gelatine in Novy jar over hydrogen	—	—	—	—	Planted 2-12 examined 2–26
Checks	+	+	+	+	

EXPERIMENT 40.—FINAL CHECK ON STERILITY OF SOLUTIONS.

Number of flask	I	II	III	IV	
Gelatine plates	—	—	—	—	Planted 3–9 examined
Gelatine tubes	—	—	—	—	Daily after 3–10 to 3–20
Beef tea tubes	—	—	—	—	
Pea-bean tubes	—	—	—	—	
Checks	+	+	+	+	
Anaerobic conditions on litmus glucose in a Novy jar over hydrogen	—	—	—	—	Planted 3–9 Examined 3–23
Checks	+	+	+	+	

EXPERIMENTS 41.

As a final check on the previous results the following tests were made: Two flasks were plugged with cotton, sterilized by dry heat for 1 minute at 200° C. To each flask 100 cc. of water and 10 grams of lime were added. They were then autoclaved 20 minutes at 110° C. Two pieces of calfskin 1 x 2 inches were sterilized 48 hours in a Seymour-Jones solution. The sterile hides were placed in the flask October 30, 1913. The flasks were left undisturbed at room temperature until March 9, 1914, when they were opened and sub-cultures made as in previous experiments. All sub-cultures were negative but the checks were positive. The flask, therefore, contained a sterile solution.

The skin had changed considerably in its 4 months treatment in sterile lime. The hair was all very loose; the upper layer and the flesh side of the skin had become mushy and swollen. The corium was fairly firm but glassy in appearance. No odor was noticeable. The preceding experiments had all been made on calfskin. In order to check the results on heavier hides a sample of sterilized cowhide was placed in a sterile lime solution Decem-

ber 12, 1913. This contained 5 grams of lime and 0.5 gram of sodium sulphide in 100 cc. of water. The hide was examined March 9, 1914. The flask had been left undisturbed during this time. Sub-cultures were made as before, and all results were negative. This showed that the solution was sterile.

This hide had also changed materially by its 3 months' treatment in sterile lime. All the hair was dissolved. The upper layer had been dissolved and the flesh side had not only become mushy as in the previous experiment, but in fact it had disappeared, leaving only a firm tough layer of corium, which had apparently suffered very little change.

Depilation in Sterile Solution and Subsequent Tannage.

After these preliminary tests of liming under sterile conditions, somewhat larger pieces of hide were used and carried through the entire tanning process. The final products were then compared with commercial products obtained by liming in the usual manner.

The first experiments were on pieces of cowhide which were tanned subsequently, through the courtesy of Mr. V. A. Wallin, in the Wallin tanneries at Grand Rapids.

Experiment 42. Experiments on Cowhides.

Two pieces of cowhide about 1 x 10 feet were sterilized 3 days in Seymour-Jones's solution. The bottles in which the previous solutions had been sterilized had been made of cheap cast glass but had caused much trouble by breaking during sterilization, in spite of the utmost precautions taken while heating and cooling them. This difficulty was overcome by using narrow and deep galvanized iron cans 5 centimeters by 42 centimeters by 46 centimeters. Small shelves were arranged so the hides could be suspended over glass rods. The solutions to be used were sterilized in these cans by boiling over a direct flame for 4 to 8 hours. The cover, not fitting tightly, allowed a cloth moistened with 0.02 per cent. mercuric chloride solution to be placed over the can in such a manner that it could be kept sterile.

Hide No. 1, was limed in a solution containing 5 grams of lime and 0.5 gram of sodium sulphide crystals, in 400 cc. of

water, for 3 days. It was removed while slightly underlimed and placed in a can containing a sterile saturated lime solution and shipped to the Wallin Tannery, Grand Rapids, Michigan, to be put through their regular tanning process.

Hide No. 2, was limed in the same kind of a solution as No. 1 but for 6 days. It was removed and shipped in a sterile saturated lime solution. Sub-cultures made as in previous experiments gave negative results and showed that these hides had been unhaired in sterile solution.

The finished sample of leather from hide No. 1 was returned from the tannery with the comment:

"The job seems to be satisfactory. The stock is a little bit snappy on the grain but it is not certain that this has any relation to the liming."

The finished sample of leather from hide No. 2 has not yet been returned from the tannery.

Experiment S-43.

Two pieces of cowhide were received wet and salted. They were washed thoroughly in water and sterilized in Seymour-Jones solution for 48 hours. The limes used were made up by dissolving 5 grams of lime and 0.5 gram of sodium sulphide in 400 cc. of water. They were sterilized by boiling 4 to 8 hours over a free flame. The hides were now treated as follows: One piece was limed 4 days, then placed in a sterile saturated lime solution and shipped to the tannery. The other piece was purposely overlimed and after 7 days in the lime was sent to the tannery in the same way as was the other piece. Sub-cultures from the limes used, were made on various media in the same manner as in previous experiments. All sub-cultures were negative and showed that the solutions had been sterile.

The loss of hide substance in the liming process is often considerable and an examination was made of some of these lime solutions to determine the amount of hide substance dissolved. For comparison an old lime from the Wallin tannery was also tested. The hide substance in solution was calculated from the content of ammonia shown by the Kjeldahl method. The results are shown in the following table:

HIDE SUBSTANCE DISSOLVED IN LIMES.

Source of lime	Ammonia g. per l.	Hide substance g. per l.	Remarks
Experiment 42	0.1366	0.623	Hide 3 days in
Hide #1.	0.1326		sterile lime.
Experiment 42	0.3145	1.457	Hide 6 days in
Hide #2.	0.3155		sterile lime.
Experiment 43	0.4114	1.909	Hide 4 days in
Hide #1.	0.4138		sterile lime.
Experiment 43	0.9479	4.376	Hide 7 days in
Hide #2.	0.9452		sterile lime.
Old lime from Wallin tan	1.439	6.694	
	1.454		

The amount of hide substance dissolved by these sterile limes is less than that shown in the old lime from the tannery but not enough is known of the changes of limes with continued use to warrant a positive conclusion.

EXPERIMENTS ON CALFSKINS.

Calfskins received in the dry salted state were unhaired in sterile limes and through the courtesy of Mr. Carl E. Schmidt, tanned by the chrome process in his Detroit tannery.

Considerable difficulty had been experienced in handling the can used to contain the sterile limes in the previous experiments, and spots appeared on the hides where they touched the metal. The calfskins were limp enough so that glass vessels could be used.

EXPERIMENT S-41A.

A bottle of about 6 liters capacity was plugged with cotton and sterilized at 200° C. for 1 minute in a dry heat sterilized. One-half of a small calfskin, weighing 250 grams was sterilized 24 hours in a Seymour-Jones solution. A lime solution containing 5 grams of lime and 0.15 gram of red arsenic sulphide in 400 cc. of water was put into the sterile bottle and this was autoclaved at 110° C. for 20 minutes. The sterile skin was now placed in the sterile lime and left for 9 days. The hair slipped very easily. This skin was sent to the Carl E. Schmidt Tannery at Detroit, Michigan, where it was chrome tanned and finished. The product was of little value. The grain could be peeled off easily. The leather had very little strength and felt very thin. The liming had been allowed to proceed too long and the skin had become seriously damaged. The grain was also drawn and harsh.

In subsequent tests on calfskin a large Jena flask of about 15 liters capacity was plugged with sterile cotton. The flask was too large to permit sterilization in a dry heat sterilizer hence it was only washed with distilled water. The cotton plug, after it was made to fit the flask was sterilized for 5 minutes at 200° C. A lime solution was made containing 5 grams of lime and 0.15 gram of red arsenic sulphide per 400 cc. of water, and put into the flask. This was then autoclaved 4 to 5 hours at 110° to 120° C.

EXPERIMENT 44.

One-half of a small calfskin was sterilized 48 hours in Seymour-Jones's solution. It was then placed in the sterile lime solution in the sterile flask and allowed to remain 5 days. The hair was partially destroyed and slipped easily, except in certain spots. These spots were very difficult to unhair for some reason. The grain of this leather cracked and scuffed easily and was not satisfactory.

EXPERIMENT 45.

The flask used in Experiment 44 containing the same lime and arsenic sulphide solution, was autoclaved 4 to 5 hours at 110° to 120° C., to insure sterility of the contents. One-half of a dry salted calfskin which had been sterilized for 24 hours in a Seymour-Jones solution, was added to the cooled flask with sterile forceps. This skin was limed 6 days. Sub-cultures made precisely as in previous experiments showed negative results and that the limes had been sterile. The skin unhaired easily except in one place an area of about 6 square inches. The white hair on this spot adhered with remarkable tenacity while the black hair on the rest of the skin slipped easily. No explanation of this peculiar occurrence could be suggested at the tannery. The hide felt "full" and the final product was of fair quality. The leather had average tensile strength and a good grain although it did not feel as full as the standard product of the tannery. Stretching did not crack the grain of the final product except on the extreme flank.

EXPERIMENT 46.

To the same lime solution in the flask of Experiment 45 9 grams of red arsenic sulphide, 300 grams of slaked lime and

enough water were added to bring the contents up to the original volume. This flask was again autoclaved 4 to 5 hours at 110° to 120° C. to insure sterility of the contents. The piece of calfskin to be used was sterilized as before in a Seymour-Jones solution for 24 hours. The hair slipped easily after 6 days. Sub-cultures made from this lime solution, on various media as in previous experiments, showed negative results and proved the solution to have been sterile. The final leather felt quite "full" in the judgment of the tannery superintendent. It had a good grain and a tensile strength greater than that of the average skin limed in the ordinary manner. It had a very slight harshness which could probably be overcome by modification of the finishing process. The leather felt very full both in the flank and at the backbone. The flank appeared to be better than in the ordinary product.

Conclusions.

The foregoing paper studies from three different viewpoints the changes taking place in hides during their conversion into leather and particularly during the liming process. A study is made of structural changes throughout the vegetable and mineral tanning processes as shown by the microscope; of gross changes in volume, weight and density of the skin; and of the practicability of carrying out the depilation process in sterile solutions.

Detailed methods have been worked out for the satisfactory preparation of microscopic sections both by the colloidin and freezing methods. A study of numerous sections of skin shows that the structural changes occurring during depilation and tannage are so gradual that only the broad outline can be followed. The inter-fibrillar substance in the bundles of connective tissue dissolves in the liming process and the fiber bundles split up into their component fibrils. The flank is composed of larger, fewer and more irregular fiber bundles with larger interstitial spaces than the better portions of the skin. This gives a partial explanation of the poorer quality of flank leather.

When dry calfskins are put into water they increase in superficial area, thickness and weight but decrease in density. The area remains almost constant during the liming process in bacterial limes, but the volume and hence the thickness of the skin increases quite consistently and at a decreasing rate during the

liming process. The weight increases at approximately the same rate but a study of the relationship of weight and volume as shown by the density curves, indicates that the volume increases faster than the weight during the first 4 or 5 days in limes containing bacteria so that at the end of this period the hide shows the minimum density which it ever attains in the limes. Within 2 days after this point is reached the volume decreases more rapidly than the weight and the density rises decidedly. The significance of these points of inflection of the curves is not evident.

Both volume and weight decrease in the feebly acid bate used but the decrease in weight is greater than that of the volume so that the density falls. In the pickle, conditions are the reverse of those in the bate and the density rises sharply. No great changes in weight volume or density occur during the one bath tannage used.

Different pieces of the same skin while the same in general, show decided quantitative variations from each other. The shoulder, back and rump show distinct differences which are not constant in different skins. The flank, however, swells quite consistently more than the rest of the skin, both in water and in the limes. These differences may be due to the varying thickness of the skin or to surface conditions such as fat. If the flesh side is painted with a soap solution before immersion in the limes so that an insoluble lime soap is precipitated upon it, the swelling is greatly increased.

It has been shown that it is possible to depilate a skin or hide under strictly sterile conditions with lime alone or with the addition of sulphides. The same sterile lime solution can be used to depilate successive pieces of hide. Calfskin kept for 6 months in sterile milk of lime shows a firm though rather glassy corium. A skin kept a similar length of time in sterile milk of lime containing arsenic or sodium sulphide, is completely dissolved. The hair from the skins in the latter solutions is also dissolved completely, while that of the skin in lime alone, appears almost unchanged.

Pieces of cowhide and calfskin unhaired under sterile conditions have been tanned and finished in commercial tanneries using vegetable and mineral tanning agents, with fair results. It seems entirely probably that with a little more experience in handling

sterile limes a good product, equal in all respects to that produced by the present methods of liming could be obtained.

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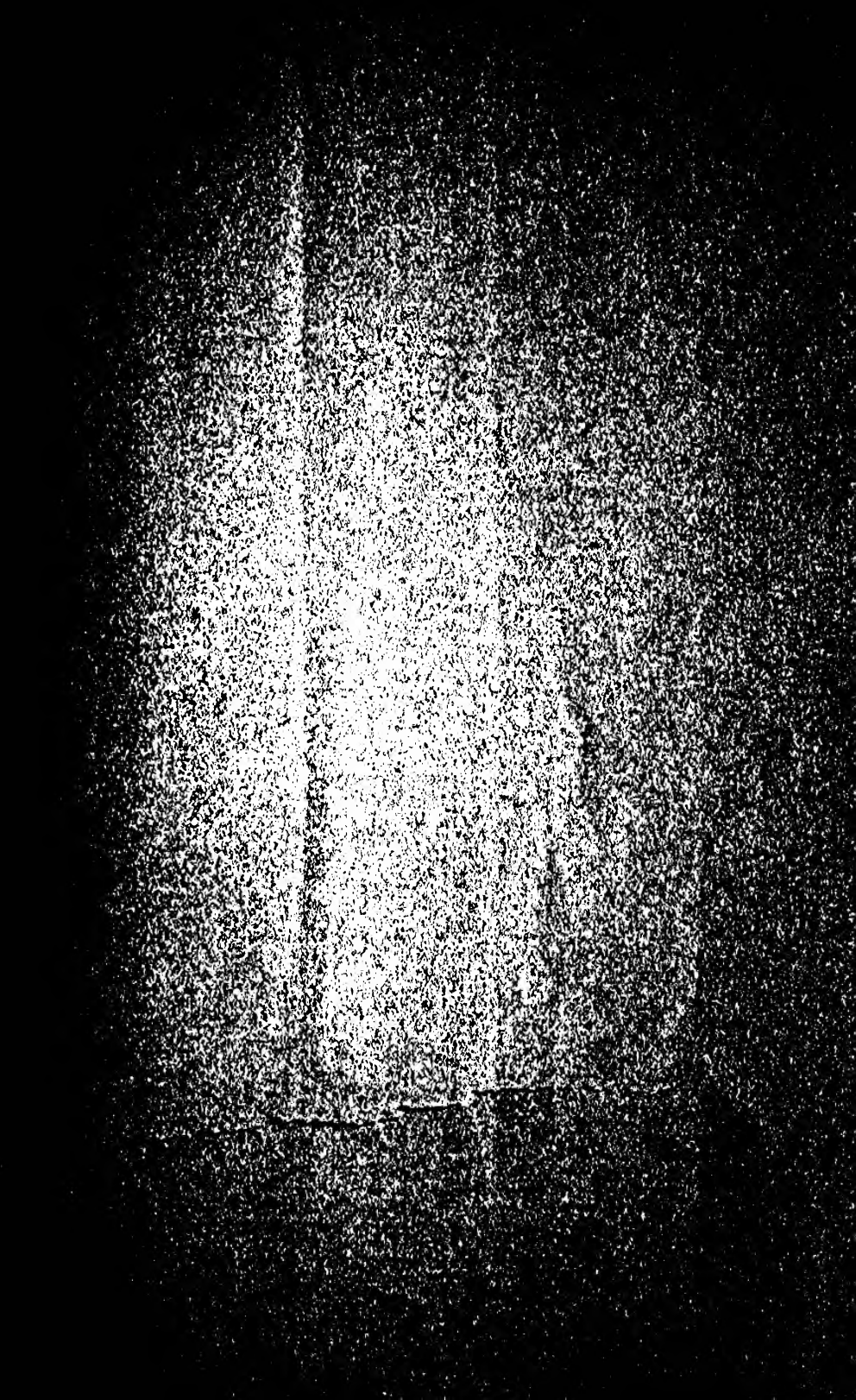

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